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Photolysis of Phoxim on Glass and on Tomato Leaves

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Phoxim (phenylglyoxylonitrile oxime 0,0-diethylphosphorothioate; volaton) is an organophosphorus insecticide with a broad spectrum of effectiveness as a contact and stomach poison (HARRIS 1970, HARRIS & SVEC 1970, JUDA & McEWEN 1970, HOMEYER 1975). It has a short residual life in soil (HARRIS 1970, DRAGER 1977) and on forage corn and grass plants (BOWMAN & LEUCK 1971). Phoxim is widely used in Egypt to control several vegetable crop pests. The purpose of the present study was to investigate the effects of heat and light on the stability of this compound. Also, the decline of the insecticide residue on and in treated tomato plants was investigated to determine the span of time which should lapse between spraying and safe marketing of treated plants under local environmental conditions.

MATERIAL AND METHODS

Exposure procedure : Phoxim was exposed to UV, sunlight, and different temperatures as a thin dry film either on uncovered Petri-dishes (2.5 cm, i.d.) or in 10-mL closed volumetric flasks. Acetone was used to transfer 2 mg of phoxim to the respective containers. Two wavelenghths of UV light were used, 254 and 350 nm. Exposure to sunlight was conducted in July 1978 (Maximum temperature ranged from 35 to 40°C). Constant temperature studies were conducted in an electric oven. After indicated intervals (table 2) , acetone was used for rinsing off the residues in two replicates of Petri-dishes or flasks. The acetone was evaporated to near dryness, known amounts of acetone were added, usually 10 mL, then aliquots were used for thin-layer chromatography (TLC) or colorimetric analysis.

Tomato plant studies : At the College of Agriculture experimental station, Cairo University, two plots (each 1/40 acre) were sprayed with phoxim at the rate of 2 kg (5% a.i.) volaton per 400 L per acre. Tomato plants were about 2 months old. A third plot was used as a control. Leaf samples, usually 50 or 100 g, were collected after several intervals (Table 3). Both the external and internal residues of phoxim were determined. External

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residues were recovered by rinsing both leaf surfaces with acetone. Acetone washings were concentrated and the residues were dissolved into benzene. To extract internal residues, leaves were macerated in a Waring blender for one min using 2 mL acetone per g sample. The macerate was filtered and cleaned-up according to the procedure of DRAGER (1971).

TLC : Glass plates (20 x 20 cm) were coated with a 0.25 mm layer of Silica Gel G. Carbon tetrachloride-chloroform (9:1, V/V) was the solvent system. Developed plates were sprayed with the color reagent DCQC (2,6-dibromo-p-benzoquinone-4-chloroimine, 0.3% in cyclohexane). Proper aliquotes of the final organic extracts were spotted on TLC plate and standard **phoxim** were spotted on another plate. After plate development, the silica gel area for **phoxim** was scraped from the samples plate, eluted with acetone through filtration, and finally subjected to colorimetric analysis.

Analysis : Phoxim was estimated by oxidation of the organic phosphorus to inorganic phosphate (NAKAMURA 1952) which was estimated colorimetrically by the method of DICKMAN & BRAY (1940).

NMR analysis : Three major degradation products, referred to as b, g, h (Fig. 1) beside the original **phoxim** (f, Fig. 1), were subjected to nuclear magnetic resonance analysis (NMR) using $CHCl_3$ as the internal standard.

RESULTS AND DISCUSSION

Chromatogram in Fig. 1A shows the effect of both heat and light treatments on the residues of phoxim. It is clear that phoxim was affected by the aforementioned factors, producing degradation products represented by five visible chromatographic spots (a, b, c, g and h) beside the **original** (f). Two of these products (g and h) appeared only after UV exposure while compound (c) was only detected on TLC plates after heat treatment.

Degradation products of phoxim, after application of **volaton** foremulation in and on tomato leaves after 2 days of weathering were recorded in Fig. 1B. On leaf surfaces only two degradation products (g and h) were detected, while in leaf extracts an additional three compounds (b, c and d) were appeared.

NMR investigation (Table 1) revealed that TLC fraction (f) was identified as unchanged parent compound. The fraction (b) contains two nonequivalent ethoxy groups at 1.2 and 3.7 ppm and no aromatic protons, suggesting a hydrolized product. The fraction (g) could not be identified with the available data. The fraction (h) seems to have two equivalent ethoxy groups at 1.2 and 3.7 ppm and no aromatic protons.

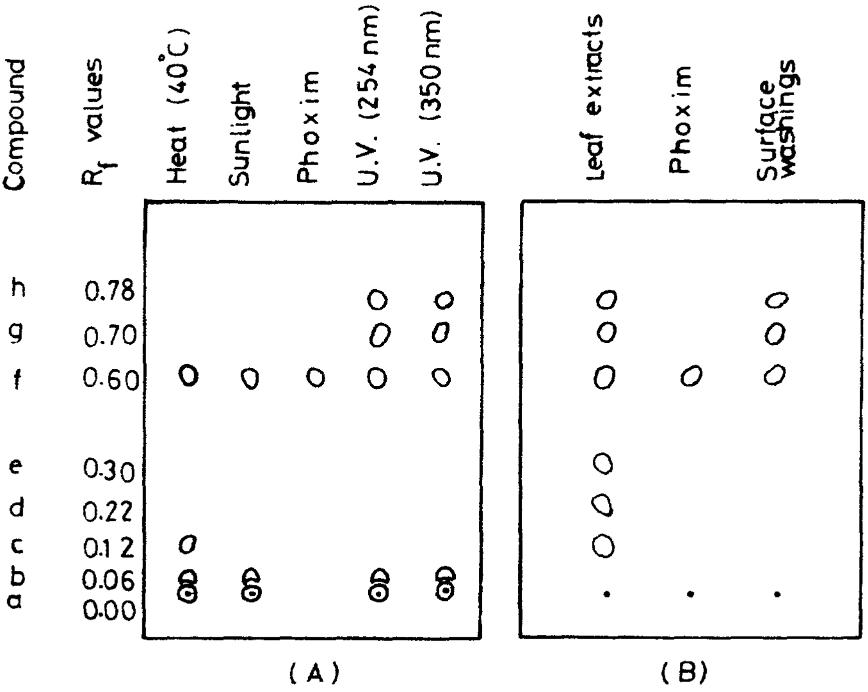

Figure (1) : Typical TLC chromatograms for phoxim degradation products on glass surfaces (A) or in tomato plants (B).

Table 1 : NMR spectral data.

TLC Fraction	Proton NMR Signal (ppm)		Remarks
	Aromatic	Aliphatic	
f	7.6 - 7.9 m	1.2T,4.2D,Q	parent compound
b*	-	1.2T,3.7 Q	nonequivalent ethoxy groups
g*	not identified		-
h*	-	1.2, 3.7	equivalent ethoxy groups

* No aromatic fraction was identified.

Qualitative data for the effect of heat on phoxim stability (Table 2) indicated that the compound was almost stable at 20 and 30°C during the 10 day period of the experiment. At a higher temperature (40°C), phoxim residues showed a remarkable decrease after only 1 day of heat exposure. The loss in phoxim residues increased with increasing length of exposure. Also, the present data indicated that the rate of the insecticide degradation at 40°C was faster when exposed in uncovered Petri-dishes than when exposed in closed volumetric flasks where the calculated half-life (t 1/2) values were 5.5 and > 10 days respectively.

Data on the effect of UV light and direct sunlight on phoxim are in Table 2. With UV irradiation, the rate of loss in phoxim residues as indicated in Table 2 was much faster when the compound was exposed to 254 nm than when exposed to 370 nm. Similar results have also been obtained for the photodegradation of other pesticides (CROSBY 1969, KNOWLES & GUPTA 1969).

Phoxim photodegradation was faster when exposed to sunlight than when exposed to UV irradiation. Calculated t 1/2 values were 0.66 and 0.74 h with sunlight exposure (Table 2), and 3.7 and > 10 h with UV irradiation (Table 2), when the chemical was exposed in uncovered Petri-dishes and closed volumetric flasks, respectively. Such data disagree with the general belief that the UV component of sunlight is responsible, in most cases, for all the photoalterations of pesticides in the environment (CROSBY 1969, MATSUMURA 1973). The present data could be explained on the basis of the heat effect. The UV exposure was conducted at 25 ± 2°C at which the compound proved to be stable (Table 2). On the other hand, the sunlight exposure was conducted outdoors during the summer season where the temperature was from 35-40°C, a range which proved to affect the persistance of phoxim residues (Table 2). Thus for UV exposure, the effect was mainly due to the UV light, while in case of sunlight exposure the effect was the result of both heat and light effects.

As in the case of heat treatment, the rate of loss in phoxim residues was much faster when the compound was exposed to either UV or sunlight as a thin dry film in uncovered Petri-dishes than when it was exposed in closed volumetric flasks. These results could be easily attributed to the effect of evaporation, and air oxidation factors which could be added to thermal and/or light effects in the case of exposure in uncovered Petri-dishes.

Generally, when the rate of phoxim photodecomposition as indicated in the present work is compared with the photodecomposition rates of other insecticides as reported by EBERLE & GUNTHER (1965), EL-REFAI & HOPKINS (1966), CROSBY (1969), and RISKALLAH et al. (1979), it seems that phoxim is less stable than many insecticides when exposed to light.

Table 2 : The effect of heat, UV, and sunlight on the chemical stability of phoxim.

Time Intervals	Percent of initial amount remaining after exposure in : Closed volumetric flasks			Uncovered Petri-dishes		
	Heat treatment					
	20°C	30°C	40°C	20°C	30°C	40°C
0	100	100	100	100	100	100
1 day	100	100	94	99	99	81
2 days	100	100	90	96	96	78
4 days	100	100	90	95	91	61
6 days	100	100	87	95	88	47
8 days	100	100	85	94	82	21
10 days	100	100	85	93	80	16
	UV treatment					
	254 nm	350 nm		254 nm	350 nm	
0	100	100		100	100	
1 h	97	97		67	91	
2 h	95	97		55	87	
4 h	95	97		47	84	
6 h	94	96		38	81	
8 h	94	95		25	71	
10 h	93	94		17	66	
	Sunlight treatment					
0	100			100		
1 h	31			26		
3 h	24			23		
6 h	22			14		
1 day	12			7		
2 days	7			5		
4 days	2			1		
5 days	ND[a]			ND		

[a] ND = < 1%

Chemical assessments for the dissipation and penetration of phoxim into tomato leaves are in Table 3. The given data indicate that the initial deposit, as determined one hour after phoxim

Table 3 : Phoxim residues (ppm) detected on and in tomato leaves following phoxim spraying.

Post-treatment intervals	Leaf surface washings	Leaf extracts
1 h	19.0	-
1 day	9.3	0.1
2 days	4.1	0.3
4 days	1.2	ND[a]
6 days	0.7	ND
8 days	0.6	ND
10 days	0.6	ND

a. ND = $<$ 0.1 ppm.

application on tomato plants was 19 ppm. About 50% of the residues disappeared from leaf surfaces within 1 day after treatment. Thereafter, phoxim residues disappeared at a relatively slower rate to reach about 3% of the initial residues after 10 days. These results are in agreement with those of FAHMY et al. (1978) working on tomato fruit and those of BOWMAN & LEUCK (1971) working on forage corn and grass and indicate the short residual life of phoxim on treated plants. Such data are also in harmony with short residual activity of phoxim in treated soil (HARRIS 1970, DRAGER 1977). On the other hand, minute amounts of phoxim could be detected in leaf extracts 1 and 2 days following phoxim spraying. These amounts were found to represent only from 0.5 to 1.5% of the initial surface residues. Four days after treatment, all the detected phoxim in leaf extracts had disappeared. Such data may indicate that phoxim has poor systemic properties. Also, it is possible that a considerable amount of phoxim may have penetrated into the tomato leaves and degraded rapidly just after penetration. This suggestion could be strengthened by the appearance of 5 degradation products in leaf products, in comparison with only 2 degradation products on leaf surfaces (Fig. 1 B).

In view of the short residual life of phoxim as demonstrated by the present work, this compound can be used safely on edible and fodder crops without any harm if the last treatment is conducted 10 days before harvesting.

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