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PHOTO SENSITIZING OR STABILIZING INFLUENCE ON TWO ORGANOPHOSPHORUS INSECTICIDES UNDER ULTRAVIOLET RAYS AND DIRECT SUNLIGHT EXPOSURES

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Abstract

This investigation was carried out to study the influence of benzoin, benzil, *P*-nitrophenol and 8-hydroxyquinoline on the rate of photodegradation of the active ingredients of diazinon and pirimiphos-methyl insecticides which are widely used in Egypt to protect vegetable crops from economic pests.

The calculated residue half lives values with UV light exposure were 13.59, 12, 24, 3.53 and 3.47 hours for diazinon alone & in presence of *p*-nitrophenol, 8-hydroxyquinoline, benzil & benzion, respectively. While these values were 8.77, 7.00, 19.80 , 0.81 and 0.82 hours for the same treatments, respectively. We conclude that the 8-hydroxy quinoline was more stabilizing agent than 4-nitrophenol. Benzil was found to be more sensitizing agent than benzoin. While 4-nitrophenol has almost the same effect that occurred when pirimiphos-methyl was applied alone, but 8-hydroxyquinoline stabilized in the insecticide by its powerful stabilizing action.

The calculated residue half life values with sun light exposure of diazinon and pirimiphos-methyl were 1.01 and 0.59 hours, while the values were 0.67, 0.6, 0.29 and 0.53 hours for diazinon and 0.42, 1.02, 0.21 and 0.29 hours in the presence of *p*-nitrophenol, 8-hydroxy quinoline benzil and benzion, respectively. The stabilizing agent in this experiment had no effect, while the sensitizing agent had the expected effect from the beginning of the experiment, including that benzil was a more powerful sensitizing agent than benzion .

INTRODUCTION

The effect of ultraviolet radiation on the rate of degradation of pesticides are influenced by some chemical agents, which facilitate the transfer of the energy (photosensitizets). This could be estimated by the use of two different wavelengths rays. The first at 254 nm from artificial light and the other one from direct sunlight having UV components above 254 nm. The mechanism of photosensitization formed by electron transfer from the singlet state of sensitizer followed by photolysis or isomerization of the ground state (charge transfer mechanism). Singlet sensitizers such as diphenyl amine were found to induce photolysis of halobenzene while triplet sensitizers such as benzophenone did not enhance the rate of reaction (Miller and Narang, 1970). Humic acid, tryptophane and tryosine, occurring in natural water, act as photosensitizers towards some kinds of pesticides in the environment (Draper and Crosby 1981).

This investigation aimed to study the influence of some photo-sensitizers or stabilizers on the rate of photodegradation of some organophosphorus pesticides irradiated by UV-ray and direct sun light.

MATERIAL AND METHODS

Pesticides

1. Diazinon (basudin, diazitol, neocidol, nucidol): 0,0-diethyl-0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate

2. Pirimiphos-methyl (actellic, actellifog, silo son, blex): (0-2-diethyl-6-methylpyrimidin-4-yl 0,0-dimethyl phosphorothioate.

Photosensitizers

1. *p*-nitrophenol.
2. Benzoin (benzol phenyl carbinol) or (∝-hydroxy ∝-phenyl acetophenone).
3. Benzil (1, 2 diphenyl ethane dione) or (dipphenyl-∝, ß-diketone).
4. 8-hydroxyquinoline

Procedure

Aliquots of tested organophosphorus insecticides repesenting one ml ethyl acetate containing 1000ug a.i. were placed into pyrex uncovered petridish 5ml in diameter and one ml of photosensitizers and photostablizer (0.1% in ethyl acetate) were added. Petridishes were gently shaken, allowed to dry, and then exposed to UV-rays (254 nm) at the distance 12 cm or direct sunlight. Samples were taken at zero time and at the intervals 1, 3 , 6, 12 and 24 hours in case of direct sunlight exposure and 1, 3, 6, 12 and 24 hours in case of UV rays exposure, respectively. Each sample was transferred quantitatively into a standard glass stoppered test tube and the solvent (ethyl acetate) was evaporated to dryness prior to determination by gas chromatography.

Determination

A Pye Unicam 4500 gas chromatograph equipped with a flame photometric detector operated in the phosphorus mode (526 filter) was used for determination of the tested insecticides. A pyrex glass column (1.5 m x 4 mm i.d.) was packed with 4 % S.E.-30 + 6% OV-210 on gas chromosorb Q (90 - 100 mesh).

Temperature degrees and gas flow rates were as follows:

Column Temp. 230 °C.
Detector Temp. 240 °C.
Injector Temp. 235 °C.

Gases flow rates were 30 ml/min. for nitrogen, hydrogen and air. Retention time for diazinon and pirimiphos-methyl under these conditions were 3.32 and 2.13 min., respectively. The half life time (t_{50}) for each of the investigated insecticides was calculated using the equation of Moye (Moye *et al.* 1987).

$t_x = \ln 2/k' = 0.6932/k'$
$k' = I/t_{x\ \ln} \,.\, a/b_x$
Where:
k' = rate of decomposition.
a = Initial residue
t_x = Time in hours.
b_x = Residue at x time.

RESULTS AND DISCUSSION

Effect of tested photosensitizers on the decomposition of the tested insecticides after exposure to UV-light

1. Diazinon: Data in Table 1 clearly showed that the rate of decomposition of diazinon residues was 20.59% after one hour from exposure to UV-rays. While the corresponding values were 24.95, 17.24, 31.16 and 36.10 % when diazinon was exposed to UV-rays in the presence of *p*-nitrophenol, 8-hydroxy quinoline, benzil and benzion for the same period of exposure, respectively. The percentage loss of diazinon after exposing to UV-rays at 24 hours was 61.61 % & 54.08, 49.98, 94.74 and 83.63 % at the same treatment, respectively. The calculated residue half life value of this insecticide was 13.59. hours, while the values became 12, 24, 3.53 and 3.47 hours in the presence of *p*-nitrophenol, 8-hydroxy quinoline, benzil and, benzion, respectively. From the

Table 1. Effect of UV-rays on the persistence of diazinon and pirimiphos-methyl when mixed with some photosensitizer and photostabilizers.

Time of exposure in hours	Diazinon		Diazinon+ 4-nitrophenol		Diazinon+ 8-hydroxyquinoline		Diazinon+ benzil		Diazinon+ benzoin	
	μg insecticide	Loss %	μg insecticide	Loss %	μg insecticide	Loss %	μg insecticide	Loss %	μg insecticide	Loss %
0	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	794.93	20.59	750.44	24.95	827.53	17.24	688.40	31.16	638.93	36.10
3	701.93	29.80	630.13	36.98	800.00	20.00	555.00	44.50	549.67	45.03
6	641.18	35.88	573.45	42.65	719.17	28.08	456.00	54.40	336.15	66.38
12	541.82	45.84	500.00	50.00	630.79	36.92	280.33	71.96	226.11	77.38
24	383.82	61.61	451.08	54.89	500.14	49.98	82.53	91.74	163.63	83.63
$t_{1/2}$ in hrs	13.59		12.00		24.00		3.53		3.47	
	pirimiphos-methyl		pirimiphos-methyl+ 4-nitrophenol		pirimiphos-methyl+ 8-hydroxyquinoline		pirimiphos-methyl+ benzil		pirimiphos-methyl+ benzoin	
	μg insecticide	Loss %	μg insecticide	Loss %	μg insecticide	Loss %	μg insecticide	Loss %	μg insecticide	Loss %
0	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	867.87	13.21	705.88	29.41	829.62	17.03	426.08	57.39	432.82	56.71
3	796.74	20.32	659.50	34.05	757.57	24.24	219.39	78.06	272.26	72.77
6	537.58	46.24	551.46	44.85	674.38	32.56	113.78	88.62	118.40	88.16
12	375.48	62.45	378.37	62.16	541.08	45.89	81.71	91.82	88.23	91.17
24	194.63	80.53	148.45	85.15	395.03	60.49	10.92	98.90	26.31	97.36
$t_{1/2}$ in hrs	8.77		7.00		19.80		0.81		0.82	

mentioned results, we conclude that the 8-hydroxy quinoline was more stabilizing agent than 4-nitrophenol. Sensitizer lead to markedly observed rate of degradation from the beginning of the experiment, benzil was found to be more sensitizing agent than benzoin.

2. Pirimiphos-methyl: The data in Table 1. represent the decomposition percentages of pirimiphos-methyl. The percent loss of Pirimiphos-methyl residues was 13.21% after one hour of exposure to UV-rays. The corresponding values were 29.41, 17.03, 58.39 and 56.71 % when Pirimiphos-methyl was exposed to UV-rays in the presence of *p*-nitrophenol, 8-hydroxy quinoline, benzil and benzion for the same period of exposure, respectively. The calculated residue half life value was 8.77 hours, while the values were 7.00, 19.80, 0.81 and 0.82 hours in the presence of the same photosensitizer. This finding indicate that benzil has the more powerful sensitizing effect than benzoin , while 4-nitrophenol has almost the same effect that occurred when pirimiphos-methyl was applied alone, however, 8-hydroxyquinoline stabilized in the insecticide due to ts powerful stabilizing action.

Effect of photosensitizers on the decomposition of the tested insecticides after exposure to direct sunlight

1. Diazinon: Data in Table 2. showed that the rate of decomposition of diazinon residues was 49.38 % after one hour from exposure to direct sunlight. While the corresponding values were 64.06, 68.36, 90.77 and 72.81% when diazinon was exposed to direct sunlight in the presence of *p*-nitrophenol, 8-hydroxy quinoline, benzil and benzion for the same period of exposure, respectively. The percentage loss of diazinon after exposing to sunlight for 4 hours was 97.67 %, but it became 96.42, 96.48, 98.86 and 96.29 % at the same period of exposure with the same treatments, respectively. The calculated residue half life value of this insecticide was 1.01 hour & 0.67, 0.6, 0.29 and 0.53 hours in the presence of *p*-nitrophenol, 8-hydroxy quinoline, benzil and benzion, respectively. The stabilizing agent in this experiment had no effect, while the sensitizing agent had the expected effect from the beginning of the experiment, including that benzil as a sensitizing agent was more powerful than benzion.

2. Pirimiphos-methyl: As shown in Table 2. the percentage loss of pirimiphos-methyl residues was 68.57 % after one hour of direct exposure to sunlight. These values became 80.71, 49.28, 96.11 and 90.57 % when the compound was exposed to direct sunlight in the presence of *p*-nitrophenol, 8-hydroxy quinoline, benzil and benzion, respectively. The half life value of pirimiphos-methyl was 0.59 hour, while it became

Table 2. Effect of sunlight on the persistence of diazinon and pirimiphos-methyl when mixed with some photosensitizer and photostabilizers.

Time of exposure in hours	Diazinon		Diazinon+ 4-nitrophenol		Diazinon+ 8-hydroxyquinoline		Diazinon+ benzil		Diazinon+ benzoin	
	µg insecticide	Loss %	µg insecticide	Loss %	µg insecticide	Loss %	µg insecticide	Loss %	µg insecticide	Loss %
0	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	506.18	49.38	359.37	64.06	316.40	68.36	92.30	90.77	271.87	27.81
3	23.23	97.67	35.80	96.42	35.14	96.48	11.40	98.86	37.06	96.29
6	0.33	99.96	0.70	99.92	0.76	99.93	0.35	99.96	2.77	99.72
12	0.16	99.98	0.13	99.98	0.04	99.99	0.22	99.97	0.85	99.91
24	0.00	100.00	0.00	100.00	0.00	100.00	0.00	100.00	0.00	100.00
$t_{1/2}$ in hrs	1.01		0.67		0.60		0.29		0.53	
	pirimiphos-methyl		pirimiphos-methyl+ 4-nitrophenol		pirimiphos-methyl+ 8-hydroxyquinoline		pirimiphos-methyl+ benzil		pirimiphos-methyl+ benzoin	
	µg insecticide	Loss %	µg insecticide	Loss %	µg insecticide	Loss %	µg insecticide	Loss %	µg insecticide	Loss %
0	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00	1000.00	0.00
1	314.28	68.57	1925.85	80.71	507.13	49.28	38.85	96.11	94.28	90.57
3	13.50	98.65	25.82	97.41	39.69	96.03	10.18	98.98	92.52	97.04
6	0.89	99.91	0.76	99.92	0.71	99.92	4.52	99.54	3.45	99.65
12	0.23	99.97	0.05	99.99	0.06	99.99	0.27	99.97	0.46	99.95
24	0.00	100.00	0.00	100.00	0.00	100.00	0.00	100.00	0.00	100.00
$t_{1/2}$ in hrs	0.59		0.42		1.02		0.21		0.29	

0.42, 1.02, 0.21 and 0.29 hours in the presence of the above mentioned photosensitizers, respectively.

Hegazy *et al.* (1999) studied the effect of acetophenone, benzoin, benzil, *p*-nitrophenol and chlorphyll compounds in methanol on the rate of photodegradation of pirimiphos-methyl, fenitrothion, malathion and prothiofos. They found that benzil and benzoin were active as photosensitizers for all the studied insecticides. Chlorophyll and acetophenone generally showed no photosensitizing effect. Only chlorophyll showed a moderate effect to both fenitrothion and prothiofos. On the other hand, *p*-nitrophenol had photostabilizing effect with pirimiphos-methyl, malathion and prothiofos, but the effect was most evident with pirimiphos-methyl. The photostability effect was clearly evident tor acetophenone with prothiofos irradiated by UV-light.

Photolysis is one of the various factors determining the fate of a pesticide in the environment. A number of studies had examined the photolysis of pesticides in water and air as well as on plant and soil surfaces by sunlight and ultraviolet light irradiation (Draper and Crosby, 1981; Wong and Crosby, 1981) Light plays an important role in the behaviour of pesticides in the environment, when the molecule which absorbs a photon becomes unstable and undergoes a variety of competing primary processes, such as chemical reaction isomerization etc., to return to a stable state (Zepp and Cline, 1977). Photosensitization occurs by the formation of the excited state charge transfer complex, by electron transfer from the singlet state of sensitizer followed by photolysis or isomerization of the ground state (charge transfer mechanism). Singlet sensitizers such as diphenyl amine have been found to induce photolysis of halobenzene, while triplet sensitizers such as benzophenone do not enhance the rate of reaction (Miller and Narage, 1970). Using photosensitizers such as acetone riboflavine, rhodamine B, chlorophyll and methylene blue results in the rapid disappearance of ETU under both natural and artificial light (Ross and Crosby, 1973). Photosensitization via energy transfer and / or photoinduced degradation of pesticides is known to occur in the presence of humic substance (Coudhry, 1982).

It has been reported that humic acid, tryptophane and tyrosine, occurring in natural water, act as photosensitizers towards some kinds of pesticides in the environment (Draper and Crosby, 1981). The excited triplet static of humic substances can transfer its energy to chemical adsorbed, but that its excited singlet plays an insignificant role due to its extremely short life time (Zepp *et al.*, 1985). One can conclude that both photosensitizing agents (e.g., humic acids or some pigments that can act in this way in nature) and iron compounds, usually occurring at levels of the order of 0.1

mg/l in surface water, can play a significant role in kinetics of photooxidative degradation of pesticides (Sedlak *et al.*, 1992). It has been reported also, that the soil transition metal catalysis and a change in the adsorption spectra of chemical in sorbed states resulted in acceleration of the photolysis (Plimmer 1972). However, the photostability of pesticides is due to the lower quantum yield and lower rate of specific sunlight absorption (Takahashi *et al.* 1985). The efficiency of photostabilization is affected by several factors. Adsorption to clays containing a minimal concentration of lattice iron was found to slow down the photo inactivation, probably due to charge-transfer processes occurring between the insecticide molecules and the Fe^{3+} ions. When the cationic dye 3,6-diamino-10-methylcridinium (AF) was coadsorbed, termolecular interaction between it and the pesticide resulted in a considerable improvement of the photostabilization yield (Rozen and Margulies 1991). The photodegradation of parathion and chlormphos insecticides can be sensitized by a number of compounds which are present in biochemical systems such as pyruvic and aketoglutaric acid (Buckland and Davidson, 1987). 2, 4, 5-trichlorophenoxy acetic acid in water was photolyzed by artificial UV-light, the rate of reaction increased twice in the presence of acetone or riboflavine as a photosensitize agent (Crosby and Wong,1973).

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تأثير المحسسات الضوئية على اثنين من المبيدات الفوسفورية المعرضة للاشعة فوق البنفسجية وضوء الشمس المباشر

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تمت دراسة تأثير البارانيتروفينول و٨-هيدروأكسى كينولين والبنزوين والبنزيل كمحسسات ضوئية عند تعرض متبقيات المبيدين الديازينون والبيريميفوس ميثايل للاشعة فوق البنفسجية وأشعة الشمس المباشرة. وأوضحت الدراسة ما يلى:

١- دلت النتائج أن نسبة الفاقد من متبقيات الديازينون والبيريميفوس – ميثايل ٤٥,٨٤٪ و٦٢,٤٥٪ بعد ١٢ ساعة من زمن التعريض لأشعة فوق بنفسجية. وأن تأثير البارانيتروفينول و٨-هيدروأكسى كينولين والبنزوين والبنزيل على نسبة من متبقيات الديازينون هى ٥٠,٠٠ و٣٦,٩٢ و٩٦,٧١ و٧٧,٣٨٪ والبيريميفوس-ميثايل ٦٢,١٦ و٤٥,٨٩ و٩١,٨٢ و٩١,١٧٪ على نفس زمن التعريض. وكانت فترات نصف العمر لمتبقيات مبيد الديازينون ١٣,٥٩ و١٢ و٢٤ و٣,٥٣ و٣,٤٧ ساعة ومبيد البيريميفوس-ميثايل ٨,٧٧ و٧,٠٠ و١٩,٨٠ و٠,٨١ و٠,٨٢ ساعة عند تعريضهما لأشعة فوق بنفسجية فى وجود وعدم وجود المحسسات الضوئية السابقة الذكر. كما أوضحت النتائج أن ٨-هيدروكسى كينولين عامل مثبط قوى وأن البنزيل عامل منشط أقوى من البنزوين.

٢- دلت النتائج أن نسبة الفاقد من متبقيات الديازينون والبيريميفوس-ميثايل ٤٩,٣٨٪ و٦٨,٥٧٪ بعد ساعة واحدة من زمن التعريض لأشعة الشمس المباشرة وأن تأثير البارانيتروفينول و٨-هيدروأكسى كينولين والبنزوين والبنزيل على النسبة المئوية الفاقدة لمتبقيات مبيد الديازينون ٦٤,٠٦ و٦٨,٣٦ و٧٧,٩٠ و٧٢,٨١ ٪ والبيريميفوس-ميثايل ٨٠,٧١ و٤٩,٢٨ و٩٦,١١ و٩٠,٧٥٪ على نفس زمن التعريض أن نسبة الفاقد من متبقيات الديازينون والبيريميفوس-ميثايل بعد أربع ساعات من زمن التعريض لأشعة الشمس المباشر تتراوح من ٩٦٪ إلى ٩٩٪ فى وجود أو عدم وجود تلك المحسسات الضوئية. وكانت فترات نصف العمر لمتبقيات مبيد الديازينون هى ١,٠١ و٠,٦٧ و٠,٦٠ و٠,٢٩ و٠,٥٣ ساعة ومبيد البيريميفوس-ميثايل ٠,٥٩ و٠,٤٢ و١,٠٢ و٠,٢١ و٠,٢٩ ساعة عند تعريضهما لأشعة فوق بنفسجية فى وجود وعدم وجود المحسسات الضوئية السابقة الذكر. كما أوضحت النتائج أنه لا يوجد عامل مثبط وأن البنزيل عامل منشط أقوى من البنزوين وذلك من بداية التعريض.