

Photodegradation of Azole Fungicide Triadimefon

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To examine the photostability of the fungicide triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1*H*-(1,2,4-triazol-1-yl)butan-2-one] in the field, model experiments with organic solvents were performed. Photolysis in methanol, hexane, and acetone resulted in considerable formation of 1-(4-chlorophenoxy)-3,3-dimethylbutan-2-one, 1-[(4-chlorophenoxy)methyl]-1*H*-1,2,4-triazole, 1*H*-(1,2,4-triazol-1-yl)-3,3-dimethylbutan-2-one, and 1-phenoxy-3,3-dimethyl-1*H*-(1,2,4-triazol-1-yl)butan-2-one. The rate of photodegradation in different solvents followed first-order rate kinetics with a significant correlation coefficient.

Keywords: *Triadimefon; photodegradation; photoproducts; solvents; rate kinetics*

INTRODUCTION

Triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1*H*-(1,2,4-triazol-1-yl)butan-2-one, first reported in 1973 by Frohberger, is reported to be a very good protectant and eradicator fungicide against powdery mildew and rust fungi (Buchenauer, 1973). It has been claimed to move systemically after application to roots or leaves of cereals (Kasper *et al.*, 1975) and basipetally in cucumber and barley (Scheinflug and Paul, 1977). Its activity is probably enhanced as a result of considerable redistribution in the vapor phase. It is also used as a foliage fungicide (Wright *et al.*, 1983) and as a soil fungicide (Hardison, 1975, 1976). Clark *et al.* (1978) studied the photolysis of triadimefon in methanol using a medium-pressure mercury vapor lamp and identified only 1*H*-1,2,4-triazole, methyl 4-chlorophenyl carbonate, and 4-chlorophenol.

To study systematically the photochemical reactivity of pesticides on plant surfaces, model photoreactions are undertaken. Hartmann and Schwack (1994) used organic solvents with selected functionalities as substitutes for components of plant waxes for photodegradation of triadimefon. In the present paper, the results of photochemical degradation of triadimefon in the presence of hexane, methanol, and acetone as representative model substances for the plant cuticle constituents are presented.

MATERIALS AND METHODS

Chemicals. A technical sample of triadimefon (95%) was supplied by M/s Bayer Ltd. (New Delhi, India) and was purified further by repeated crystallization from *n*-hexane to constant melting point (80–81 °C) and shown to be chromatographically pure (TLC, GLC, and HPLC). The solvents used were of analytical grade.

Apparatus and Chromatography. Triadimefon and its degradates in rate kinetics studies were analyzed with a GLC instrument (Hewlett Packard Model 5890, series II gas liquid chromatograph, equipped with an electron capture detector and a capillary column [HP-1, methyl silicon gum, 10 m × 0.53 mm i.d. × 2.63 μm film thickness], coupled with a Hewlett Packard 3390A integrator). The operating conditions were as follows: oven, injector, and detector temperatures at 160, 250, and 300 °C, respectively. Nitrogen was used as carrier gas with a flow rate of 20 mL min⁻¹. The ultraviolet–visible spectrum of triadimefon was recorded on a Hitachi Model V-2000 double-beam UV–vis spectrophotometer in methanol using a quartz cuvette (1 cm path length). The infrared spectra of products were recorded on a Nicolet Impact-700 FT-

IR spectrophotometer. ¹H-NMR spectra were recorded on a Varian EM 360L (60 MHz) instrument. Deuteriochloroform (CDCl₃) or carbon tetrachloride (CCl₄) was used as solvent and tetramethylsilane (TMS) as the internal standard for NMR. Gas chromatography–mass spectroscopy was done on a HRDC-MEGA 2 series, coupled with a Fisons-TRIO 1000 ion trap mass spectrometer. The ionization potential was 70 eV. The GC was equipped with a SE-54 capillary column (15 m × 0.25 mm i.d., film thickness, 0.1–0.15 μm). The conditions were as follows: initial temperature was 60 °C for 1 min and then heated up to 250 °C (10 min) at 15 °C min⁻¹. Helium was used as the carrier gas.

TLC was performed on 20 × 20 cm² glass plates coated with 0.5 mm silica gel G, using iodine as chromogenic reagent. Photoproducts were separated by column chromatography using a glass column (75 cm × 2 cm i.d.) containing 500 g of 60–100 mesh preactivated silica gel in *n*-hexane and eluting with hexane and hexane and acetone in different ratios.

Irradiation and Photoproducts. Solutions of triadimefon (100 ppm) in hexane, methanol, and acetone, respectively, were irradiated for 24 h with a medium-pressure Hg lamp (125 W, Phillips) and a water-cooled quartz filter. After irradiation, the solvent was distilled off under reduced pressure. To produce enough of photoproducts for structural analysis, triadimefon was irradiated in five different batches.

Preparation of Comparison Compounds. Pinacol hydrate and pinacolone were synthesized according to the procedure described by Vogel (1989).

1-Bromo-3,3-dimethyl-2-butanone (1-Bromopinacolone). Bromine (5 mL; **Caution:** experiment should be carried out in a fume cupboard, using gloves and facemask), dissolved in glacial acetic acid (10 mL), was added dropwise to a solution of pinacolone (10 g) in acetic acid (10 mL) with constant stirring and maintaining the temperature (25 °C). After addition of bromine, stirring was continued for another 2 h. The solution was extracted with *n*-hexane and dried over sodium sulfate. Hexane was distilled off, and product was distilled at 71 °C at 10 mmHg. The IR spectrum of the product showed the presence of C=O at 1719 cm⁻¹. ¹H-NMR (CCl₄): δ 4.1 (s, 2H, CH₂), 1.3 (s, 9H, C(CH₃)₃).

1-(4-Chlorophenoxy)-3,3-dimethylbutan-2-one. A solution of 1-bromopinacolone (100 mg) and 4-chlorophenol (300 mg) was refluxed in dry benzene (10 mL, experiment should be conducted in fume cupboard) in the presence of anhydrous potassium carbonate (1 g) for 4 h. The solution was filtered to remove potassium carbonate. The benzene layer was separated and treated with sodium hydroxide solution (10%) to remove excess phenol. It was washed several times with water. The benzene layer was dried over anhydrous sodium sulfate. On distillation, a yellow oil was obtained which solidified on standing; mp 63–65 °C. It was purified by column chromatography. The IR spectrum of the product showed the presence of a carbonyl group at 1728 cm⁻¹. ¹H-NMR (CDCl₃):

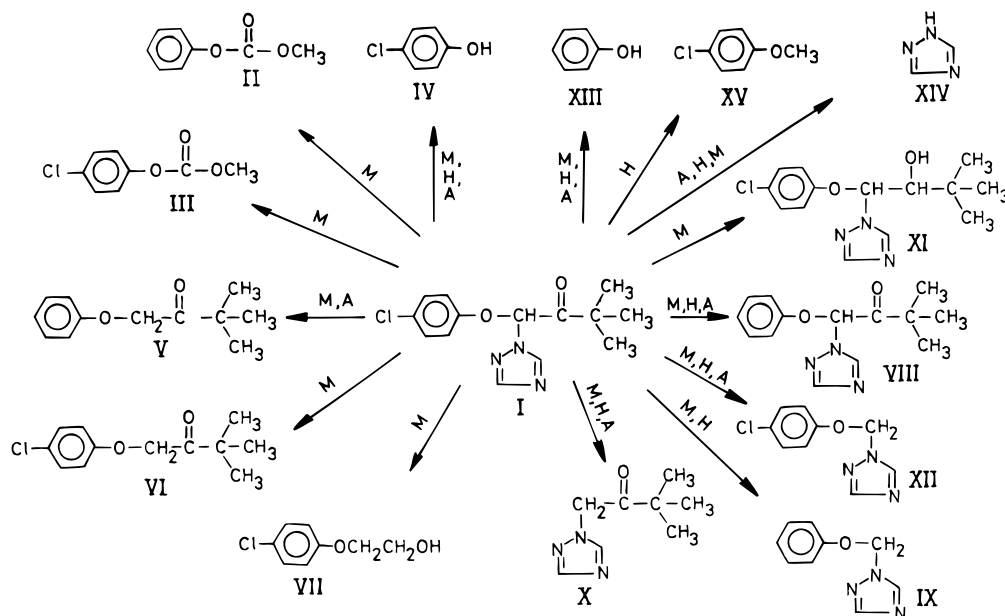


Figure 1. Possible photodegradation products of triadimefon (**I**) in methanol (M), *n*-hexane (H), and acetone (A).

δ 7.2 (d, 2H, AA'BB, aromatic), 6.8 (d, 2H, AA'BB, aromatic), 4.6 (s, 2H, CH₂), 1.1 (s, 9H, C(CH₃)₃).

1H-(1,2,4-Triazol-1-yl)-3,3-dimethylbutan-2-one. A solution of 1,2,4-triazole (200 mg) and 1-bromopinacolone (600 mg) was refluxed in dry acetone in the presence of anhydrous potassium carbonate (1 g) for 4 h. The solution was filtered to remove potassium carbonate. The filtrate was evaporated to dryness. The residue was subjected to column chromatography. A solid thus obtained was crystallized from methanol as a colorless amorphous solid. The IR spectrum of the product showed the presence of a carbonyl group at 1731 cm⁻¹. ¹H-NMR (CDCl₃): δ 8.2 (s, 1H), 7.9 (s, 1H), 5.3 (s, 2H, CH₂), and 1.2 (s, 9H, C(CH₃)₃).

Photolysis Kinetics. A solution of triadimefon (10 ppm, 20 mL) in solvents (methanol, acetone, and hexane) was irradiated in quartz and Pyrex tubes under UV light. Samples were withdrawn at intervals of 0, 0.5, 1, 3, 5, and 7 h from quartz tubes and 1, 3, 5, 8, 12, 16, 20, 24, 30, 36, and 48 h from Pyrex tubes and analyzed by GLC.

RESULTS AND DISCUSSION

Isolation and Identification of Photoproducts (Figure 1). **(i) Photolysis in Methanol.** A methanolic solution of triadimefon (**I**, 1000 ppm) was irradiated for 24 h. The solvent was removed by rotary vacuum evaporation, and the residue was subjected to column chromatography over activated silica gel. Photoproducts were separated by successive elution with hexane and hexane-acetone in different ratios. The separated photoproducts were further purified either by crystallization from appropriate solvent or by the preparative TLC. The following photoproducts were identified by IR, ¹H-NMR, MS, GC-MS, and comparison with authentic standards.

Methyl Phenyl Carbonate (II). TLC: *R_f* 0.93 (solvent system, *n*-hexane-acetone, 95:5 v/v). MS: *m/z* 152 (fragments recorded in Table 1).

Methyl 4-Chlorophenyl Carbonate (III). TLC, *R_f* 0.85 (solvent system, *n*-hexane-acetone, 9:1 v/v). MS: *m/z* 186 (M⁺) (**III**, Figure 1, Table 1), base peak at *m/z* 127/128 (M⁺ - 59).

4-Chlorophenol (IV). mp: 43 °C. bp: 217 °C. ¹H-NMR (CDCl₃): δ 7.8 (s, 4H, aromatic). MS: *m/z* 128/130 (M⁺). Identified by Co-TLC, Co-GLC, and mmp comparison with an authentic sample.

1-Phenoxy-3,3-dimethylbutan-2-one (V). MS: *m/z* 192 (M⁺).

1-(4-Chlorophenoxy)-3,3-dimethylbutan-2-one (VI). mp: 63-65 °C. The IR spectrum of the photoproduct showed the presence of carbonyl group at 1728 cm⁻¹. MS: *m/z* 226 (M⁺) (**VI**, Table 1). Its ¹H-NMR, IR, and mass spectra were comparable with those of an authentic sample.

2-(4-Chlorophenoxy)ethanol (VII). MS: *m/z* 172, 171 (base peak), 27/128 (**VII**, Table 1, Figure 1).

1-(Phenoxy)-3,3-dimethyl-1H-(1,2,4-triazol-1-yl)butan-2-one (VIII). The IR spectrum of the product showed a band at 1720 cm⁻¹, indicating the presence of a carbonyl group. The ¹H-NMR spectrum showed two one-proton singlets at δ 8.2 and 8.0, corresponding to two triazole protons. It also showed a multiplet at δ 7.8, corresponding to five aromatic protons, a singlet at δ 6.9 for one proton at C-1, and a singlet at δ 1.2 for nine protons of the *tert*-butyl group. MS: *m/z* 259 (M⁺) (Table 1).

1-(Phenoxy)methyl-1,2,4-triazole (IX). MS: *m/z* 175 (M⁺) (Table 1), 69, and 95. The mass spectrum showed the absence of chlorine atom.

1-(1,2,4-Triazol-1-yl)-3,3-dimethylbutan-2-one (X). The IR spectrum of the product showed the presence of a carbonyl group at 1731 cm⁻¹. The ¹H-NMR spectrum of the product showed two singlets for one proton each at δ 8.2 and 8.0 for two triazole protons, a singlet of two protons at δ 5.3 for CH₂, and nine proton singlet at δ 1.2 for the *tert*-butyl group (Figure 1). MS: *m/z* 167 (M⁺) (Table 1). The product was identified by Co-TLC, Co-IR, and comparison of the mass and NMR spectra with those of an authentic sample.

1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-ol (XI). The product was identified by comparison of its IR, NMR, and mass spectra with those of an authentic sample.

1-[(4-Chlorophenoxy)methyl]-1,2,4-triazole (XII). The IR spectrum of the product showed the absence of carbonyl group. The ¹H-NMR spectrum showed the presence of two one-proton singlets at δ 8.3 and 8.0 for two triazole ring protons. It also showed four aromatic protons at δ 7.4-7.2. The NMR spectrum showed the absence of a singlet at δ 1.2 due to the *tert*-butyl group.

Table 1. Mass Spectral Data of Photodegradation Products of Triadimefon

product	mass found (<i>m/z</i>)	abundance (%)	structure	yield (%)
I	293	18	M ⁺	15.0
	258	10	M ⁺ - Cl	
	236	12	M ⁺ - C(CH ₃) ₃	
	208	100	M ⁺ - O=C-C(CH ₃) ₃	
	166	15	M ⁺ - <i>p</i> -chlorophenoxy	
II	127/128	80	ClC ₆ H ₅ O*	1.0
	152	80	M ⁺	
	121	100	M ⁺ - OCH ₃	
III	93	80	C ₆ H ₅ O*	2.0
	186	70	M ⁺	
	155	20	M ⁺ - OCH ₃	
IV	127	100	ClC ₆ H ₅ O*	15.0
	128	100	M ⁺	
V	192	15	M ⁺	4.5
	177	100	M ⁺ - CH ₃	
	135	35	M ⁺ - C(CH ₃) ₃	
	57	70	⁺ C(CH ₃) ₃	
VI	226	35	M ⁺	9.5
	169	28	M ⁺ - C(CH ₃) ₃	
	141	60	M ⁺ - O=C-C(CH ₃) ₃	
	127	65	ClC ₆ H ₅ O*	
VII	172	90	M ⁺	2.5
	171	100	M ⁺ - H	
	155	80	M ⁺ - OH	
	141	30	M ⁺ - CH ₂ OH	
	127	40	ClC ₆ H ₅ O*	
VIII	259	8	M ⁺	4.5
	202	10	M ⁺ - C(CH ₃) ₃	
	174	100	M ⁺ - O=C-C(CH ₃) ₃	
	93	45	C ₆ H ₅ O*	
IX	175	100	M ⁺	2.5
	147	95	M ⁺ - N-CH ₂	
	93	40	C ₆ H ₅ O*	
X	167	10	M ⁺	10.5
	110	15	M ⁺ - C(CH ₃) ₃	
	82	80	M ⁺ - O=C-C(CH ₃) ₃	
	69	15	1,2,4-triazole	
XI	295	15	M ⁺	11.0
	260	10	M ⁺ - Cl	
	208	12	M ⁺ - CHOHC(CH ₃) ₃	
	127	20	ClC ₆ H ₅ O	
	209	95	M ⁺	
XII	141	50	M ⁺ - 1,2,4-triazole	15.0
	127	95	ClC ₆ H ₅ O	
	82	100	M ⁺ - CH ₂ -C ₂ H ₂ N ₃	
	94	100	M ⁺	
XIII	69	80	M ⁺	1.0
	42	50	M ⁺ - NCH	
XIV	142	100	M ⁺	0.5
	127	95	M ⁺ - 15	

MS: *m/z* 209/211 (M⁺), indicating the presence of a chlorine atom in the molecule (Table 1).

Two minor products were identified by GC-MS of the irradiated solution. They were identified as phenol (**XIII**) and 1,2,4-triazole (**XIV**) (Figure 1, Table 1).

(ii) Photolysis in Hexane. A solution of triadimefon (500 mg) in hexane (500 mL) was irradiated in quartz tubes for 48 h. The solvent was distilled under vacuum, and the residue showed the formation of a number of photoproducts on TLC. It showed the formation of **IV**, **VIII**, **IX**, **X**, **XII**, **XIII**, and **XIV** by comparison of their NMR and mass spectra with those of photoproducts obtained earlier.

Elution of the column with *n*-hexane-acetone (97:3 v/v, fractions **I**-**V**) gave a colorless liquid. Its mass spectrum showed a molecular ion peak at *m/z* 142 (Table 1). It was tentatively identified on the basis of mass spectrum as methyl 4-chlorophenyl ether (**XV**, Figure 1).

(iii) Photolysis in Acetone. A solution of triadimefon (500 mg) in acetone (500 mL) was irradiated in

quartz tubes for 48 h. NMR and mass spectra of isolated products were in good agreement with photoproducts **IV**, **V**, **VIII**, **X**, **XII**, **XIII**, and **XIV** identified earlier (Table 1, Figure 1).

The UV spectrum of triadimefon (**I**) in methanol and water exhibited a band at 225 nm for allowed π - π^* transition of the phenyl ring and a band at 274 nm, which is essentially *n*- π^* in character, resulting from the combined transitions of the carbonyl system and lower energy band of the aromatic rings. These π - π^* and *n*- π^* transitions can lead to the production of either singlet or triplet excited states. Thus, no unique excited state can be invoked to explain the variety of photoreactions undergone by the various functional groups of triadimefon.

Figure 1 shows the possible degradation products of triadimefon. The photoproducts identified can be rationalized as originating from any one of the following photochemical processes (A-E) (Figure 2).

The photochemical cleavage via pathway A (Figure 2) involves bond breaking between phenolic oxygen and the C-1 carbon atom (**Ia**), leading to the formation of two radicals. These two radicals abstract protons from the medium and yield 4-chlorophenol (**IV**) and 1-(1,2,4-triazol-1-yl)-3,3-dimethylbutan-2-one (**X**).

Pathway B (Figure 2) involves bond breaking between C-1 and C-2 yielding **Ib** and is evidently the preferred pathway in solution phase photolysis based on the yield of the products observed. The radical **Ib** abstracts a proton from the solution and yields **XII**. A similar product was identified by Hartmann and Schwack (1994) when triadimefon was irradiated in 2-propanol.

Pathway C (Figure 2) involves breaking of the bond between C-1 and N-1 (**Ic**). The radical so formed gives products **VI** and **XIV** by abstraction of protons from the medium. These photoproducts were earlier identified by Clark *et al.* (1978).

The carbonyl group of triadimefon undergoes reduction to give photoproduct **XI** (triadimenol), which also shows fungicidal activity.

Photoproduct **XV**, which was identified only when triadimefon was irradiated in hexane solution, may be formed by breaking the bond between C-1 and N-1 of photoproduct **XII** and subsequently abstracting a proton from the solvent. Photoproduct **III** was also detected by Clark *et al.* (1978) on irradiation of triadimefon in methanolic solution under UV light.

Triadimefon (**I**) and photoproducts **III**, **VI**, and **XII** undergo dechlorination to give **VIII**, **II**, **V**, and **IX**, respectively.

(iv) Rate Kinetics. The rate of photodegradation of triadimefon in solvents such as methanol, hexane, and acetone was studied under UV light from a medium-pressure Hg lamp using a quartz filter (254-316 nm). No degradation occurred in the dark, since 98% of triadimefon was recovered unchanged after 24 h. The rate of photodegradation in methanol, hexane, and acetone followed first-order kinetics with a significant correlation coefficient ($r = 0.99$). Half-lives were found to be 2.83 h, 2.49 h, and 36.70 min in methanol, hexane, and acetone, respectively (Figure 3). Photodegradation was more in acetone solution than in the presence of methanol and hexane. Methanol and hexane can be considered as a protecting solvents due to their tendency to shift the UV absorption maxima to the shorter wavelength, thus reducing molar absorptivity at 270 nm

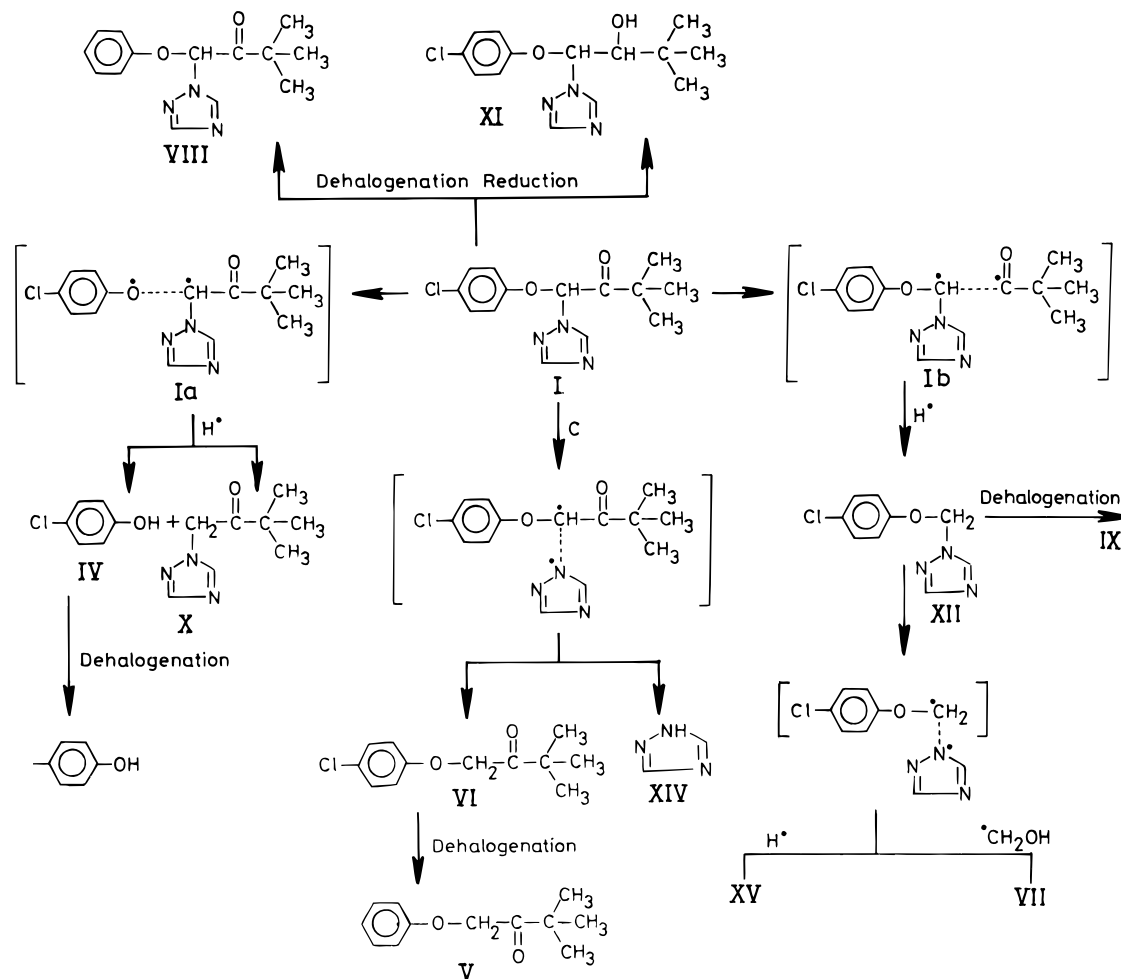


Figure 2. Proposed photochemical pathways to account for the observed photoproducts.

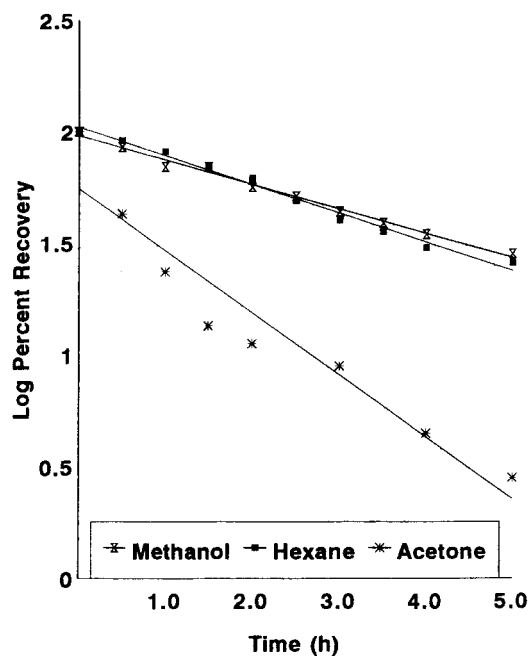


Figure 3. Linear plot for first-order rate kinetics of triadimefon in different solvents.

and giving slow degradation, whereas acetone acts as a triplet sensitizer and thus enhances the rate of degradation.

Conclusion. Irradiation of triadimefon in different solvents under UV light has given basic information

about photoreactivity, photoproducts, and possible photochemical pathways in the environment. Buchel *et al.* (1975) stressed the importance of the stability of the C-1 of triazole with respect to the biological activity of triadimefon. But we have observed that, during photolysis of triadimefon, cleavage of this bond does occur. Thus, the formation of different products as a result of irradiation in different solvents simulating environmental conditions showed the possibility of detoxification of triadimefon in the field as a result of photolysis. We can conclude that there will be a rapid breakdown of triadimefon on the leaf surface of non-fungitoxic compounds.

LITERATURE CITED

- Buchel, K. H.; Meiser, W.; Kramer, W.; Grewe, F. *Reports and Informations*, Section 3, Chemical Control, 8th International Plant Protection Congress, Moscow, 1975, Part 1, p 111.
- Buchenauer, H. *Mitt. Biol. Bundesanst. Land-Forstwirtschaft., Berlin-Dahlem* **1973**, 151, 154.
- Clark, T.; Clifford, D. R.; Deas, A. H. B.; Gendle, P.; Watkin, A. M. *Photolysis, Metabolism and other factors influencing the performance of triadimefon as a powdery mildew fungicide.* *Pestic. Sci.* **1978**, 9, 497-506.
- Frohberger, P. E. *Mitt. Biol. Bundesanst. Land-Forstwirtschaft., Berlin-Dahlem* **1973**, 151, 61.
- Hardison, J. R. Control of *Puccinia striiformis* by two new systemic fungicides. Bay Meb 6447 and BAS 31702. *Plant Dis. Rep.* **1975**, 59, 652-655.
- Hardison, J. R. Control of stripe and flag smut in Kentucky blue grass by a new systemic fungicide BAY MEB 6447. *Crop Sci.* **1976**, 14, 769.

- Hartmann, M.; Schwack, W. Fungicides and photochemistry from model to field experiments. *Book of Abstracts*, 8th IUPAC Int. Congress of Pesticide Chemistry, Washington, July 4–9, 1994, Vol. 1, p 350.
- Kasper, H.; Grewe, F.; Brandes, W.; Scheinflug, H.; Buchel, K. H. 1,2,4-Triazole derivatives, a new class of protective and systemic fungicides. *Reports and Informations*, Section 3, Chemical Control, 8th Int. Plant Protection Congress, Moscow, 1975, Part I, p 398.
- Scheinflug, H.; Paul, V. On mode of action of Triadimefon. *Neth. J. Plant Pathol.* **1977**, *83*, 105–111.
- Vogel, A.I. *Textbook of Practical Organic Chemistry*, 5th ed.; ELBS/Longman: 1989; pp 527–528.

- Wright, F. E.; Verser, J. W.; Gipson, R. D. Selective control of various foliar pathogens in wheat using fungicides. *Phytopathology* **1983**, *73*, 802.

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