Photodegradation of Pesticides. Photolysis Rates and Half-Life of Pirimicarb and Its Metabolites in Reactions in Water and in Solid Phase

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The photodegradation of Pirimicarb under three different artificial lights and sunlight was studied in water solutions (buffers pH 5, 6, and 7) and in solid phase. Five photocompounds were formed in solution and two in solid phase. Pirimicarb undergoes fast degradation under all conditions. In buffer solutions it first gave three compounds with a kinetic parallel process. These compounds were assigned the structures of 2-[(methylformyl)amino]-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**II**), 2-(methylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**III**), and 2-(dimethylamino)-5,6-dimethyl-4-hydroxypyrimidine (**V**). **V** and **II** were stable to further photolysis (the latter with $t_{1/2}$ = 849 h) whereas **III** undergoes further degradation to 2-amino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**IV**), and to 2-(formylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**IX**). Both compounds were photodegraded to undetectable species, and **IX** shows a very high $t_{1/2}$ (48 h). A different behavior was found in solid phase, and only **II** and **III** were formed. A kinetic parallel process was demonstrated. The environmental $t_{1/2}$ and $t_{1/100}$ calculated for Pirimicarb and its photoproducts suggest their reduced persistence in natural waters.

Keywords: *Pirimicarb; photodegradation; kinetics*

INTRODUCTION

Pirimicarb (**I**, Figure 1), 2-(dimethylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate, is a selective systemic insecticide that is widely employed against aphids with a contact action. It penetrates the leaves but is not translocated extensively (Tomlin, 1994). Soil-applied Pirimicarb was taken up by roots of many plants (e.g., lettuce), translocated through the xylem system, and degraded by metabolism to give **II**−**VII** (FAO/WHO, 1977). Similar transformation products (mainly **II** and **III**) were also present in water solutions of Pirimicarb after photoirradiation, and in addition, traces of 1,1-dimethylguanidine and 1-methylguanidine were found (FAO/WHO, 1977).

Romero *et al.* (1994) have reported data on the photochemical degradation of Pirimicarb in water and solid phase under artificial light and sunlight. Their data were not in agreement with FAO/WHO data (1977) and, in part, with the preliminary photochemical data reported by Cabras (1995). Thus, while Romero found **II**, **III**, **V**, and a new compound (**VIII**), no photodegradation was observed by Cabras on peach and nectarine fruits, whereas he found **II** and **III** after Pirimicarb's exposition to natural sunlight as a thin-layer film. In this work we studied in further detail the photodegradation of Pirimicarb both in buffered aqueous solutions and in solid phase. Our goal was to define the photochemical behavior of Pirimicarb and its photoproducts from a kinetic viewpoint.

EXPERIMENTAL SECTION

Chemicals. Pirimicarb (**I**) and its derivatives 2-[(methylformyl)amino]-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**II**), 2-(methylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**III**), and 2-amino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (**IV**), 2-(dimethylamino)-5,6-dimethyl-4-hydroxypyrimidine (**V**), 2-(methylamino)-5,6-dimethyl-4-hydroxypirimidine (**VI**), and 2-amino-5,6-dimethyl-4-hydroxypyrimidine (**VII**) were analytical standards (purity >98%) kindly supplied by ICI Italia (Milan, Italy). 2-[(Methylformyl)amino]-5,6-dimethyl-4-hydroxypyrimidine (**VIII**) was prepared from **II** by mild hydrolysis with stoichiometric amounts of methanolic NaOH (3% w/v) at room temperature. After 4 h the solvent was removed under reduced pressure. The crude oil was found to be a 1:1 mixture of **III** and **VIII**. The products were separated by semipreparative high-performance liquid chromatography (HPLC; see Isolation of Photoproducts).

The phosphate buffers at pH 6.0 and 7.0 were prepared with Na_2HPO_4 and KH_2PO_4 (both 0.067 M), whereas the pH 5 buffer was prepared with Na_2HPO_4 (0.2 M) and citric acid (0.1 M) (Celentano and Monticelli, 1977); the pH was adjusted with 0.10 M NaOH.

Acetonitrile, dichloromethane, diethyl ether, ethyl acetate, and acetone were HPLC grade solvents (Carlo Erba, Milan, Italy). Pyridine (>97%, AnalGrade) and cellulose thin layers (thickness 0.02 mm) were also from Carlo Erba. Humic acids (>95%), *p*-nitroacetophenone (PNAP, >98%), and 1,1-dimethylguanidine sulfate (97%) were purchased from Aldrich (Milan, Italy); water was distilled twice and purified on a MilliQ apparatus (Millipore, Milan, Italy) before use. The actinometer solution was prepared according to Dulin and Mill (1982) with PNAP at the concentration of 1×10^{-5} M.

Apparatus. The following equipment was used in this study. *High-pressure liquid chromatography*: modular systems Varian 5020 (ID 1 Varian, Palo Alto, CA), HP 1050 (ID 2, Hewlett-Packard, Milan, Italy), Spectra Physics 8700 (ID 3, Spectra Physics, Milan, Italy), fitted with variable-wavelength detectors. Their outputs were connected to a diode array detector (LC-235 with LCI-100 computer integrator, Perkin Elmer, Newark, CT). ID 1, ID 2, and ID 3 were also provided with a Valco AH-20 (loop 100 μL) injector or automatic autosampler (loop 100 μL) and connected with HP 3390 A integrators. *Analytical HPLC columns*: C_8 Spherisorb, 250 × 4.6 mm i.d., 5 μm, (Waddinxveen, The Netherlands). *Semipreparative HPLC column*: Econosil C_8, 250 × 10 mm i.d., 10 μm (Carlo Erba). *Mobile phase systems*: several mobile phases at different percentages of CH_3CN/buffer (10^{-2} M KH_2PO_4 containing 5.0 mL/L acetic acid) were employed at the flow rate of 1.0 (analytical) and 3.0 (semipreparative) mL/min. Percentage composition of eluent mixtures, retention times, and wavelengths employed were reported in Table 1. *Gas chromatography−mass spectrometry*: GC−MS Hewlett-Pack-

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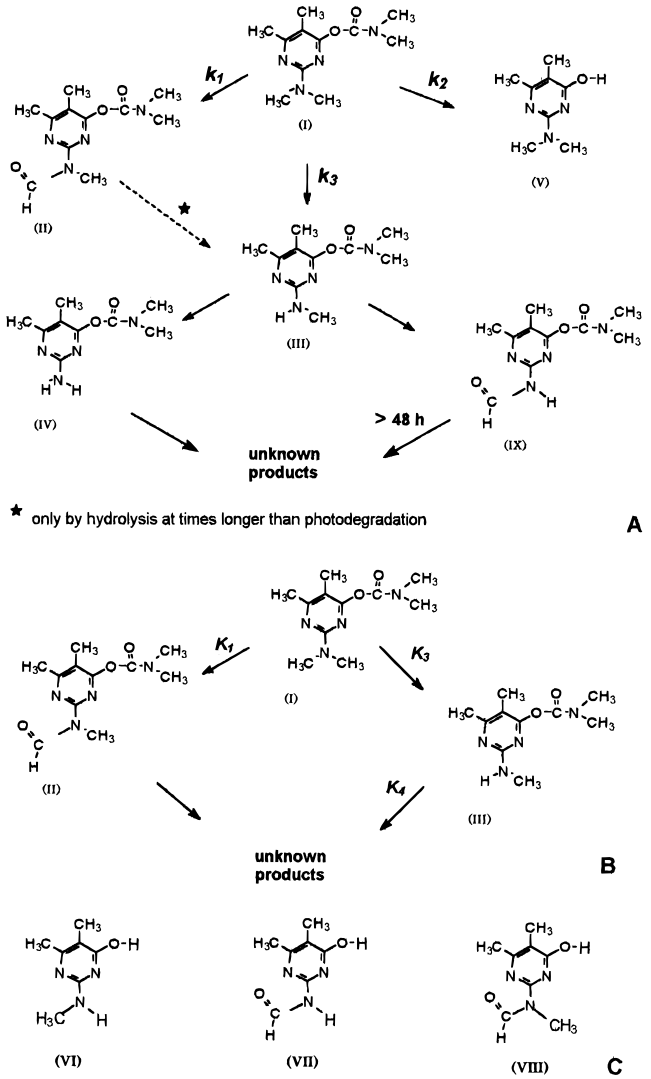

Figure 1. Behavior of Pirimicarb photodegradation in solution (A) and in solid phase (B). (C) Formulas of Pirimicarb derivatives known in the literature.

Table 1. HPLC Retention Times (min) and λ_{max} (nm) in the Analytical and Semipreparative[a] Separation of Pirimicarb and Its Photolytic Products with Different CH_3CN/Buffer (% v/v) Ratios in the Mobile Phase

	analytical		semipreparative	
compd	35:65	25:75	25:75	λ_{max} (nm)
I	10.0	15.1	21.4	236
II	8.0	18.2	36.3	245
III	5.9	9.5	11.5	230
IV	4.4	6.7	8.8	230
V	3.9	5.0	nd[b]	226
VIII	nd[b]	4.3	5.5	230
IX	4.7	8.4	15.5	237

[a] See Experimental Section for the columns employed. [b] Not determined.

ard 5890-5971, at 70 eV using electron impact ionization. *GC conditions*: Hewlett-Packard capillary column HP-5 (coated with 5% phenyl ethyl silicone, 30 m × 0.25 mm i.d., film tickness 0.25 μm); injector temperature 50 °C; carrier gas helium; temperature program 50−260 °C, 10 °C/min. Sample injection 2 μL. *NMR*: Varian VXR-300 spectrometer equipped with a Sun computer 3/60 at 300 and 100 MHz for ^1H and ^{13}C, respectively. *UV*: Varian DMS 90 UV/vis spectrometer. *IR*: FT-IR 2000 Perkin-Elmer spectrometer.

Chromatography. The calculation of the concentration in the chromatograms was made by external standard method by plotting peak height vs concentrations.

Light Sources. The lamps were calibrated with PNAP solutions (1×10^{-5} M) by three replicate experiments of photodegradation in water. The following lamps were used: (A) low-pressure mercury lamp (50 W, Helios Italquartz, Milan Italy; $I_\lambda = 4.01 \times 10^{-7}$ EL^{-1} s^{-1}) with $\lambda_{max} = 254$ nm; (B) high-pressure mercury lamp (125 W, Helios Italquartz; $I_\lambda = 4.62 \times 10^{-7}$ EL^{-1} s^{-1}) with a water-cooled quartz filter; (C) high-pressure mercury lamp (125 W, Helios Italquartz; $I_\lambda = 3.97 \times 10^{-7}$ EL^{-1} s^{-1}) jacketed with a water-cooled pyrex; this lamp emitted only the wavelengths >290 nm.

Irradiation. In all experiments nonirradiated samples were held in the dark as control. Each experiment was duplicated with four replications.

(*A*) *Under Artificial Lights.* (*1*) *In Solution.* The irradiation in buffered solutions (pH 7.0, 6.0, and 5.0) were performed as follows.

The lamps were suspended into a cylindric vessel ($v = 350$ mL, pathlength (l) = 1.2 cm) and the solution was stirred with a magnetical stirrer. The solutions of exposed compounds were at concentrations ranging between 1.0 and 3.0 mg/L [$(4.2-12.6) \times 10^{-6}$ M). Samples from reaction solutions were injected into the chromatograph without any further sample preparation.

At pH 7.0 some experiments were performed by flushing N_2 into the reactor to check the dependence of Pirimicarb's degradation by the content of O_2. In these cases, the nitrogen was bubbled into the solution before irradiation for 45 min and a flow at a pressure of 0.2 μPa kept during the time of experiment.

(*2*) *In Solid Phase.* A 0.5 mL aliquot of a solution in ethyl ether (5 mg/L, 2.0×10^{-5} M) was placed into 2.0 mL borosilicate screw-capped vials; the solvent was evaporated to dryness under a gentle nitrogen stream and the vials were suspended into a black cylinder containing the lamp with the Pyrex jacket (lamp C). At selected times one vial was withdrawn from the cylinder, frozen at −25 °C for 10 min, and finally taken up with 1.0 mL of eluting mixture (35% CH_3CN/65% buffer) and injected for HPLC analysis.

(*B*) *Under Natural Sunlight.* The outdoor experiments were carried out in February 1994 by exposing the test chemicals and the actinometer to natural sunlight at 39°14′ latitude north and 3°20′ longitude west from the Rome Monte Mario meridian.

(*1*) *In Solution.* Twenty screw-capped vials of borosilicate containing 1.0 mL of buffered (pH 7.0) Pirimicarb or photoproduct solution were exposed. The vials were withdrawn at random at selected times, and the samples injected into the chromatograph without any further sample preparation.

(*2*) *In Solid Phase.* Three different exposure experiments were performed. In the first the same procedure reported above (A2) was followed.

In the second experiment, 0.5 mL of an ethereal solution (5 mg/L) was placed in uncovered borosilicate Petri dishes. The solvent was evaporated and dishes were exposed. The dry samples were redissolved with 1.0 mL of eluting mixture and injected.

In the third experiment, 0.5 mL of the ethereal solution of compounds was adsorbed on cellulose thin layers (5 × 5 cm). The area of deposition was marked with a pencil and exposed to natural sunlight. At selected times the thin layer was drawn, and the area of cellulose scraped with a lancet into a beaker. Acetone (1 mL) was added to the cellulose powder. The resulting suspension was sonicated for 5 min and filtered with filter paper. The filtrate was evaporated under N_2 at room temperature, redissolved with 1.0 mL of eluting mixture, and analyzed by HPLC. Recovery assays performed with known amounts (4.2×10^{-6}, 8.4×10^{-6}, and 12.6×10^{-6} M) of studied compounds shows recoveries ranging between 93 and 105%.

Isolation of Photoproducts. The photoproducts were isolated from the reaction solutions as follow. After irradiation up to two half-lives ($t_{1/2}$), the solution (350 mL, concentration about 5×10^{-3} M), was placed in a separatory funnel and shaken twice with ethyl acetate (500 mL each). After drying on anhydrous sodium sulfate, the combined organic layers were evaporated under reduced pressure and temperature

Table 2. NMR, FT-IR, and GC−MS of Isolated Photoproducts

compd	^{1}H NMR[a]	^{13}C NMR[a]	GC t_r[b]	mass spectral fragmentation[e]	FT-IR data[d]	UV (nm, λ; ϵ)
I	1.97, s, CH_3 on C-3	np[c]	np[c]	np[c]	np[c]	244; 34362.9
	2.35, s, CH_3 on C-4					265; 23354.3
	3.05, d, CH_3 on NCO					270; 4000.3
	3.10, s, CH_3 on NCC					290; 5333.9
II	2.04, s, CH_3 on C-3	np[c]	10.03	253, M^+; 8	1731, C=O in −O−CO−N=	240; 29297.5
	2.38, s, CH_3 on C-4			224, $M^+ - 2CH_3$; 32	1680, C=O in CHO	258; 14119.3
	2.97, d, CH_3 on NCO			207, $M^+ - 3CH_3$; 72		270; 10236.5
	3.24, s, CH_3 on NCC			152, $M^+ - N(CH_3)_2$ CH_3NCHO, 43		290; 2117.9
	9.66, s, H of COH			72, $CON(CH_3)_2$; 100		
III	1.99, s, CH_3 on C-3	np[c]	np[c]	np[c]	3285, N−H	234; 29198.6
	2.33, s, CH_3 on C-4				1716, C=O in −O−CO−N=	245; 18837.8
	3.06, d, CH_3 on NCO					270; 3767.6
	3.10, s, CH_3 on NCC					290; 6279.3
	4.98, s, NH					
IV	1.94, s, CH_3 on C-3	np[c]	np[c]	np[c]	np[c]	np[c]
	2.30, s, CH_3 on C-4					
	3.04, d, CH_3 on NCO					
	4.98, s, NH					
IX	2.05, s, CH_3 on C-3	169.04, N*C*=O	17.64	238, M^+; 2	3290, NH	239; 51355.5
	2.38, s, CH_3 on C-4	36.61, N(CH_3)$_2$		195, $M^+ -$ NHCHO; 4	1720, C=O in O−CO−N=	250; 46686.6
	3.04, d, CH_3 on NCO	163.10, N*C*HO		165, $M^+ - OCON(CH_3)_2$; 10	1689, C=O in NCHO	270; 18674.7
	7.86, s, NH			138, $M^+ - OCON(CH_3)_2 -$ CO + 1, 65		290; 933.7
	9.35, s, H of COH			72, $CON(CH_3)_2$; 100		
VIII	np[c]	29.00, N*C*H_3	12.64	152, $M^+ -$ CHO; 15	3580, OH	226; 2773.4
		163.51, N*C*HO		124, $M^+ - N(COH)CH_3$; 76	1705, C=O in NCHO	250; 1773.4
						270; 2080.1
						290; 742.9

[a] ppm from TMS. Spectra were registered in $CDCl_3$ solution. Only **VIII** was in CD_3CN solution. [b] min; for conditions see Experimental Section. [c] Not performed. [d] cm^{-1}; Nujol. [e] *m/z*, identification; % rel abundance.

(<40 °C) until dry. The crude oil was dissolved in 3.0 mL of an acetone/water mixture (1:1, v/v) and injected (200 μL for each injection) into a semipreparative C_8 column eluted with a CH_3CN/buffer (25:75, v/v) mixture at a flow rate of 3.0 mL/min. The retention times of the compounds collected are in Table 1.

The compounds were extracted from the eluent mixture as follows. The aqueous solution (e.g., 10 mL) was saturated with NaCl (5 g). Acetone and dichloromethane were added in volumes twice that of water (or mobile phase). The mixture was shaken in a rotatory stirrer for 10 min at 50 rpm. The organic layer was withdrawn, dried with anhydrous Na_2SO_4, filtered, and then evaporated under N_2.

Identification of Isolated Photoproducts. The isolated photoproducts were identified by ^{1}H and ^{13}C NMR, GC−MS, FT-IR, and UV analysis. Spectroscopic data are collected in Table 2.

Kinetics. The kinetic studies were performed by HPLC analysis.

The constant rates of disappearance of compounds and photoproducts (K_{obs}), were calculated as pseudo-first-order constants by the equation

$$I = I_0 e^{-kt} \quad (1)$$

Each sampling time represented four replicate experiments and each determination was duplicated. The values of K_{obs} show a SD ranging between ±4.6 and 8.1.

The statistical data were calculated by a computer program (Microsoft Excel 5). The same computer program was employed for the interpretation of the parallel process according to Frost and Pearson (1961) by the equations

$$[I] = I_0 e^{-k_t T} \quad (2)$$

$$[II] = \frac{I_0 k_1}{k_t}(1 - e^{-k_t T}) \quad (3)$$

$$[III] = \frac{I_0 k_3}{k_t}(1 - e^{-k_t T}) \quad (4)$$

$$[V] = \frac{I_0 k_2}{k_t}(1 - e^{-k_t T}) \quad (5)$$

[where I_0 was the starting concentration of Pirimicarb, T the time (s), and $k_t = k_1 + k_2 + k_3$. are (see Figure 1A) the three rate constants of the single steps of the parallel process and $k_t = k_{obs}$ of the disappearance of Pirimicarb. In the case of a first-order reaction, when at $t = 0$ the starting concentrations of **II**, **III**, and **V** are zero, the concentrations of formed compounds were in proportion to their rate constants independently of the time, **II**:**III**:**V** = k_1:k_2:k_3.

Photochemical Parameters. The environmental measured rate constant (K_E^m) and $t_{1/2}$ and $t_{1/100}$ were calculated from the following equations, according to Weerasinghe et al. (1992).

$$K_E^m = k_p^c(\text{hos})/2.2$$

$$t_{1/2} = \ln(2)/K_E^m$$

$$t_{1/100} = 4.605/K_E^m$$

where $k_p^c = K_{obs}$ and hos = hours of sunlight. The daily average hours of sunlight during our experiments were 11.0. The sunlight reaction quantum yield of photodegradation (Φ_ϵ^c) and the maximum predicted environmental photolytic rate constant (K^c_E) were calculated by the following equations (Choudhry and Barrie Webster, 1985).

$$\Phi_E^c = \left(\frac{K_p}{K_p^a}\right)\left(\sum \epsilon^a \lambda L \lambda / \Sigma \epsilon \lambda L \lambda\right)\Phi_E^a \quad (6)$$

$$K_E^c = \Phi_E^c \sum \epsilon \lambda L \lambda \quad (7)$$

where K_p and K_p^a were, respectively, the degradation rate constants of the compound and of the actinometer. The terms $\sum \epsilon^a \lambda L \lambda$ and $\sum \epsilon \lambda L \lambda$ (see Table 6) represent the sum of molar absorptivity times solar irradiance for the actinometer and compounds, respectively. Φ^a_E was the reaction quantum yield

Table 3. K_{obs} ($\times 10^{-5}$ s^{-1}) for the Degradation of Pirimicarb and Its Photoproducts in Buffers under Lamps A, B, and C and Sunlight

compd	pH	K_{obs}	r^2	$t_{1/2}$ (h)
		Lamp A		
I	7.0	24.1	0.985	0.8
II	7.0	0.13	0.977	148
II	6.0	0.11	0.948	175
		Lamp B		
I	7.0	110.2	0.993	0.16
		Lamp C		
I	7.0	2.4	0.997	7.9
	6.0	1.6	0.996	11.9
II	7.0	0.023	0.998	849
	6.0	0.015	0.975	1284
III	7.0	2.5	0.999	7.6
IV	7.0	2.4	0.963	8.0
IX	7.0	0.38	0.975	48
		Sunlight		
I	7.0	7.1	0.944	2.7
II	7.0	0.08	0.945	226
III	7.0	8.0	0.981	2.3
IV	7.0	2.4	0.963	8.0
IX	7.0	1.0	0.942	19

of the actinometer (Choudhry *et al*., 1985). Solar irradiance values were taken from the Cagliari Astronomical Observatory (University of Cagliari, Cagliari, Italy) data recorded at days of sunlight experiments.

RESULTS AND DISCUSSION

In all the experiments, no degradation was observed after 1 week in the blanks stored in the dark.

Irradiation in Buffer Solutions. (*1*) *At pH 7.0.* Pirimicarb (**I**) undergoes fast degradation in buffer solutions when irradiated with the three lamps. The rate of degradation seems to be dependent on the nature of the light, as reported in Table 3. The maximum rate was observed with lamp B, while the minimum was achieved with the lamp C. This indicates that the wavelengths 254−290 nm were the most active in degradation according to the absorbances of Pirimicarb and the I_λ of the lamps.

In all experiments we found five photoproducts. The HPLC retention times and UV spectra of four compounds indicate that these are **II**−**V**. The signal at t_r = 8.4 min (Table 1) shows a UV spectrum different from those of known metabolites of Pirimicarb. To this compound, separated from the reaction medium by semipreparative HPLC chromatography, on the basis of ^1H and ^{13}C NMR spectra, GC−MS fragmentation, and FT-IR spectrum (Table 2), could be assigned the structure of 2-(formylamino)-5,6-dimethyl-4-yl dimethylcarbamate (**IX**).

In our experiments, under all artificial or natural irradiation, signals attributable to the 1,1-dimethylguanidine, and to photoproducts **VI** and **VII** (FAO/WHO, 1977) or **VIII** (Romero *et al*., 1994), were never detected in the chromatograms (see Figure 1C). The photodegradation of Pirimicarb under lamp C was very similar to those observed in natural sunlight experiments, with the photoproducts **III** and **V** appearing first followed by the photoproduct **II**. The signals of **II** and **V** always increase during the disappearance of Pirimicarb. Photoproduct **III** undergoes further degradation and the signals of **IV** and **IX** appear. During the first three $t_{1/2}$ of Pirimicarb degradation, the increase in the concentration of **IV** and **IX** is not linear. Later (**IV**) disappeared with a rate constant similar to that of Pirimicarb, while (**IX**) photodegraded slower ($t_{1/2}$ = 48 h, Table 3). Both give unknown products.

The five photoproducts were contemporaneously present in the chromatograms at times relative to the rate constants found under the different lamps. The sum of the concentrations of photoproducts formed in the different experiments was almost stoichiometrically equivalent to the disappearance of Pirimicarb (see Table 4).

To check this behavior, photocompounds **II**, **III**, **IV**, and **IX** were irradiated individually under lamp C. **II** undergoes very slow photodegradation (k_{obs} = 2.27 × 10^{-7} s^{-1}, $t_{1/2}$ = 849 h). It does not give **III**, and no other peak was present in the chromatograms. Moreover if **II** should give **III**, this could not be detected because it is photodegraded with a k_{obs} 100-fold higher (see Table 3). Photoproduct **III** may came from **II** only by hydrolysis after very long times, certainly longer than those of photodegradation. As a matter of fact, we found **III**, in the concentration of about 15%, in blanks stored in the dark of the formylamino derivative only after 24 days.

The compound **V** was not extensively studied because, by preliminary experiments, it was found very stable to photoirradiation with $t_{1/2}$ similar to that of **II**, and no signals of its degradation compounds were found in the chromatograms.

When pure specimens of **III** were irradiated, photoproducts **IV** and **IX** were formed.

Experiments performed by flushing N_2 into the reactor show meaningful variation in K_{obs} values. This indicates that the photochemical decomposition of Pirimicarb is independent of the O_2 contents in the buffer, and consequently, no free radical reaction was active (Pusino *et al*., 1992).

(*2*) *At pH 6.0.* With lamp C the behavior was similar to that at pH 7.0. The same photoproducts were formed and only the formation of **II** was contemporary with **III** and **V**. Therefore this finding does not allow us to consider the formylamino derivative as the intermediate of **III**, as suggested by Romero *et al*. (1994). Indeed, **II** is more stable to photodegradation than Pirimicarb or **III** (Table 3). Yet, the signal of **III** and also that of **II** increase up to the half-time of Pirimicarb degradation. This indicates that the reaction cannot be a consecutive process because, if it were, the signal of **III** would be not present in the chromatograms because its degradation rate was 111-fold higher than that of **II**.

The pathway could be described kinetically (Figure 1A), as a set of *two parallel* reactions. First from Pirimicarb to **II**, **III**, and **V**; then from **III** to **IV** and **IX**.

We have applied the kinetic model for a parallel process (Frost and Pearson, 1961) to our experiments from **I** to **II**, **III**, and **V**, from t = 0 to t = 165 min. Since at 165 min the signals of **IV** and **IX** were not present in the chromatograms, the second parallel reaction can be regarded as negligible. As shown in Table 7, the concentrations of **II**, **III**, and **V**, are in constant ratio with each other according to the theory.

The behavior of the photodegradations was the same under different pH and artificial lights. In the buffer solutions irradiated with lamp C at different pHs the rate of disappearance of **I** (K_{obs} × 10^{-5} s^{-1}) was found to decrease nonlinearly from 2.4 at pH 7, to 1.6 at pH 6, and to 1.2 at pH 5.

Irradiation in Solid Phase. In Petri dishes, cellulose plates, and vials exposed to sunlight, **I** always undergoes a very fast degradation to give only photoproducts **II** and **III**. Under prolonged irradiation, **IV** and **IX** were

Table 4. Comparison of the Concentrations ($\times 10^{-6}$ M) of Photoproducts Formed in Pirimicarb Degradation at pH 7.0 under Different Lamps at Times Proprotional to the K_{obs}

lamp	sampling time (min)	I	II	III	IV	V	IX	Σ	I_0	Δ%
A	75	13.90	1.55	15.80	2.09	2.79	2.58	38.70	35.90	7.80
B	20	9.58	2.44	17.40	2.44	2.50	2.99	37.50	34.30	9.33
C	1350	6.41	5.56	3.79	2.17	1.77	3.06	22.80	23.70	−3.80

Table 5. K_{obs} ($\times 10^{-5}$ s^{-1}) and Half-Life ($t_{1/2}$, min) for the Degradation of Pirimicarb, II, and III Exposed to Natural Sunlight and to Lamp C in Solid Phase

		Pirimicarb		II		III	
light	solid phase	K_{obs}	$t_{1/2}$	K_{obs}	$t_{1/2}$	K_{obs}	$t_{1/2}$
ne[a]	Petri dishes	120.5	10	ne[a]	ne[a]	ne[a]	ne[a]
sun	cellulose plates	60.5	19	ne[a]	ne[a]	ne[a]	ne[a]
ne[a]	vials	33.9	33	ne[a]	ne[a]	ne[a]	ne[a]
lamp C	vials	18.2	64	1.5	785	16.9	68

[a] Not exposed.

not formed and signals at the retention times of **VIII** and 1,1-dimethylguanidine never appear.

Under lamp C the degradation rate was slower than that in solution and the formation of **II** increased up to 190 min. At this time Pirimicarb was 25% of the starting concentration. **III** increased up to 60 min and then decreased. When **II** and **III** were irradiated alone, **III** showed a half-life similar to that of Pirimicarb, while **II** was degraded with a rate 11 times slower (Table 5). These data indicate that, in solid phase, Pirimicarb degraded with a parallel process in which, $K_1 = 1.1 \times 10^{-4}$ s^{-1} and $K_3 = 0.71 \times 10^{-4}$ s^{-1}. In a simulation of the parallel process from Pirimicarb to **III** and **II** (Frost and Pearson, 1961) up to the beginning of the degradation of **III** to unknown products, a very good agreement was reached between the theoretical and experimental concentration data (Table 7). Consequently, we suggest the pathway reported in Figure 1B for the degradation of Pirimicarb in solid phase.

The degradation rate constants under sunlight in uncovered Petri dishes, cellulose plates, and screw-capped vials were different (Table 5). The lower degradation rate found in the vials could be explained on the basis of the absorption of light by glass. The degradation in vials under lamp C was slower than that under sunlight.

In the literature it has been reported that a major pathway of loss of Pirimicarb was its volatilization (FAO/WHO, 1977). In our experiments with uncovered Petri dishes, we found that the disappearance behavior of Pirimicarb was the same of that in screw-capped vials; therefore, it was not due to volatilization but to degradation.

Environmental Photodegradation Calculations. The environmental rate constants, $t_{1/2}$ and $t_{1/100}$ in the buffer solutions at pH 7 were calculated according to the literature (Choudry and Webster, 1985; Weerasinghe *et al.*, 1992). Table 6 shows data for Pirimicarb, **II**, **III**, and **IX**. A good accordance between the calculated and measured parameters was achieved. These data indicate that only **II** could persist in natural waters. However, many photochemical sensitizers, such as humic acids, acetone, etc. (Choudhry *et al.*, 1979, 1985), could be present in natural waters. As previously described in buffer solutions the irradiation of **II** in the presence of acetone (1% w/v) or humic acids (10 mg/L) gives an increase in K_{obs} values by a factor of 10^4. Therefore photoproduct **II** should be also weakly persistent in natural waters.

Table 6. Environmental Rate Constants, Reaction Quantum Yield (Φ_a[c]),[a] Half-Lives, and $t_{1/100}$ for Pirimicarb and Its Major Photoproducts

compd	K_p (h^{-1})[b]	$\Sigma\epsilon\lambda L\lambda$[c]	Φ_E	K_E ($days^{-1}$)	$K_E{}^m$ ($days^{-1}$)[d]	$t_{1/2}$ (days)	$t_{1/100}$ (days)
I	0.25	284.53	0.075	2.13	1.25	0.55	3.68
II	0.003	0.78	0.033	0.026	0.015	46.2	307
III	0.29	132.83	0.019	2.52	1.45	0.48	3.17
IX	0.04	0.26	1.32	0.34	0.20	3.46	23.0

[a] By eq 6; $K_p{}^a = 1.6 \times 10^{-3}$ h^{-1}; $\Sigma\epsilon^a\lambda L\lambda = 81.02$. [b] K_p from Tables 3 and 5. [c] Calculated in the range 297.5−400 nm from experimental molar absorptivities. Irradiance values ($L\lambda$ meinstein per cm^2 day) were supplied by Cagliari Astronomical Observatory and refer to the exposure period, February 16−21, 1994. [d] Daily average hours of sunlight in February were 11.0.

Table 7. Comparison between Irradiation by Lamp C of the Experimental (Exp) and Calculated[a] (Cal) Concentrations ($\times 10^{-6}$) vs Time and of Experimental Concentration Ratios Found in the Pirimicarb Degradation in Solid Phase and Experimental Concentration Ratios in Buffer Solution at pH 7 for Photoproducts II, III, and V

	concns in solid phase								
time	II		III		V		exp concn ratio		
(min)	Exp	Cal	Exp	Cal	Exp	Cal	**II/III**	**III/V**	**V/II**
30	1.02	1.4	2.52	2.59	nf[b]	nf[b]	0.4	*c*	*c*
45	1.83	1.99	3.61	3.60	nf[b]	nf[b]	0.5	*c*	*c*
60	2.79	2.51	4.29	4.45	nf[b]	nf[b]	0.6	*c*	*c*

time	exp concn ratio in buffer			time	exp concn ratio in buffer		
(min)	**II/III**	**III/V**	**V/II**	(min)	**II/III**	**III/V**	**V/II**
80	0.70	1.84	0.77	130	0.76	1.97	0.67
100	0.74	1.86	0.73	165	0.79	1.97	0.64

[a] By eqs 2−5. [b] In solid phase **V** was not formed. [c] Ratios not computable.

CONCLUSIONS

When exposed to artificial light and to sunlight, Pirimicarb always undergoes quick decomposition with a kinetic parallel two-step behavior in buffer solution and a one-step behavior in solid phase. The degradation mechanism in solution does not seem a free-radical process.

The difference in the wavelengths of the lamps only affects the degradation rate constants. In the first step in aqueous solution, the main photoproducts were **II**, **III**, and **V**, the same previously reported (FAO/WHO, 1977). Photoproducts **II** and **V** were more stable than **III**. In the second step, **III** undergoes a further parallel degradation to **IV** and to the new photoproduct **IX**. Photoproducts **IV** and **IX** also undergo slow photodegradation to unknown products. Disappearance of **II** was increased by photosensitizers such as acetone or humic acids by a 10^4 factor on rate constants. The degradation data in the solution suggest a moderate persistence of **I** and its photoproducts in environmental waters.

In solid phase Pirimicarb was not lost by volatilization from uncovered Petri dishes or cellulose plates. The degradative behavior of **I** was similar in aqueous solution and solid phase in the first step but in aqueous solution **V** was also formed. The results from this work

disagree, in part, with those by Romero *et al*. (1994). We think the differences in indoor experiments could be due to differences between the lamps used by us and the Suntest apparatus in Romero's experiments. However, the differences in the disappearance rates of Pirimicarb in aqueous solutions under sunlight could be attributable to the different solar irradiances at the two latitudes (39° N vs 48° N).

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