Phototransformation of Chlorimuron-ethyl in Aqueous Solution

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Chlorimuron-ethyl is relatively stable in water buffered to pH 7.0 and 9.0, but hydrolyzes readily (half-life, 14 d) in water buffered to pH 4.0. In addition, chlorimuron-ethyl photodegrades rapidly and extensively in aqueous solution. The predominant photoproducts are 4-methoxy-6-chloro-2-aminopyrimidine, ethyl 2-aminosulfonylbenzoate, *N*-(4-methoxy-6-chloropyrimidin-2-yl)methyl urea, and *o*-benzoic sulfimide (saccharin). A minor deesterified product (chlorimuron) was evident. The decrease in chlorimuron-ethyl concentration in aqueous solutions followed first-order kinetics. The rate of degradation in different types of water followed the order irrigation water > tap water > distilled water. Chlorimuron-ethyl photodegraded in pH 4, 7, and 9 buffer solutions under both UV and sunlight. A faster degradation rate in pH 4.0 buffer solution was observed.

Keywords: *Chlorimuron-ethyl; aqueous solution; photolysis*

INTRODUCTION

Chlorimuron-ethyl (ethyl 2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate) is degraded in the agricultural environment primarily via pH- and temperature-dependent chemical hydrolysis and is not readily susceptible to other modes of degradation (Beyer et al., 1988). Earlier studies have shown that selective nonionic surfactants altered the photolysis rates of chlorimuron-ethyl in aqueous solution and on glass slides exposed to sunlight (Thomas and Harrison, 1990a,b). Following eight days of exposure, there was a 30% loss of aqueous chlorimuron-ethyl in control solutions with no surfactants, compared with a 97% loss of chlorimuron-ethyl in aqueous solution containing 0.1% (v/v) octoxynol. The presence of *p*-coumaric acid delayed chlorimuron-ethyl photolysis, whereas riboflavin sensitized its photolysis (Thomas and Harrison, 1990a; Venkatesh et al., 1993). However, no information on the identities of the degradation products has been reported.

The present study was undertaken to determine the kinetics of sunlight and ultraviolet (UV) light photodegradation of chlorimuron-ethyl in water, the products of photodegradation, and the effect on photodegradation rate of various solutes including dissolved organic matter.

MATERIALS AND METHODS

Chemicals. A technical sample of chlorimuron-ethyl (95% purity) was supplied by DuPont Far East Inc., New Delhi, India, and was purified further by repeated crystallization from benzene and hexane until a constant mp of 185 °C was achieved. Laboratory grade reagents and solvents were procured locally. All the solvents were dried and distilled before use.

Water. The types of water used in the experiments were distilled water (double distilled from systronic model distilled water plant), tap water (collected from New Delhi Municipal Corporation water supply), and irrigation water (collected from an irrigation well on Research Farm, Indian Agricultural Research Institute, New Delhi, India). The properties of the water are described in Table 1.

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Table 1. pH and EC of Different Types of Water

	distilled water	tap water	irrigation water
pH	7.00	8.44	8.70
EC (dS/m)	0.02	1.92	2.01

Preparation of Aqueous Solution of Chlorimuron-ethyl. An analytical sample of chlorimuron-ethyl (1 g) was added to 1 L of double-distilled water in a conical flask and stirred for 24 h at room temperature. The stirred aqueous solution of chlorimuron-ethyl was filtered through Whatman No. 42 filter paper. Similarly, solutions of chlorimuron-ethyl were prepared in tap water and irrigation water. The concentration of chlorimuron-ethyl was adjusted to 10 ppm by further dilution with the respective types of water.

Buffer. The buffer solutions used during the photolysis rate study to maintain pH values of 4.0, 7.0, and 9.0 were prepared according to the system established by Clark and Lubs (Lange, 1961). The buffered solutions at pH 4.0 and 7.0 were prepared by addition of appropriate amounts of 0.2 M disodium hydrogen phosphate to 0.1 M citric acid, and the buffered solution at pH 9.0 was prepared by adding 0.05 M sodium tetraborate to 0.1 M boric acid.

Aqueous Stability. The aqueous stability of chlorimuron-ethyl was characterized prior to photochemical degradation experiments. The stability of chlorimuron-ethyl (10 ppm) was tested in natural water buffered to pH 4.0, 7.0, and 9.0 (by the addition of appropriate buffer). The test solutions were maintained in the dark at 28 °C for 20 days. One 2-mL aliquot was taken from each buffer solution after 6 h and 1, 2, 3, 5, 7, 10, 12, 15, and 20 days. All experiments were done in duplicate and analyzed by HPLC-UV.

Irradiation and Photoproducts. An aqueous solution of chlorimuron-ethyl (50 ppm) was irradiated for 2 h with a medium-pressure Hg lamp (125 W, Philips) jacketed with a water cooled quartz filter. After irradiation, the aqueous solution was extracted with methylene chloride (100 mL × 3). To produce enough of the photoproduct for structural analysis, a solution of 500 mg of chlorimuron-ethyl in 5 L of distilled water was irradiated in five batches (100 mg in 1000 mL) for 2 h through a quartz filter. The irradiated solutions were combined and extracted with methylene chloride (100 mL × 9). After drying with anhydrous Na_2SO_4, the organic phase was concentrated under reduced pressure. A brown residue was obtained. A dark control experiment was performed by covering the flask with aluminum foil to ensure that a given product was derived by photochemical reactions.

Photolysis Kinetics. Aqueous solutions of chlorimuron-ethyl (distilled water, tap water, and irrigation water; 10 ppm) were irradiated in both quartz and Pyrex tubes under both

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Table 2. Hydrolysis of Chlorimuron-ethyl

	chlorimuron-ethyl, %		
dark time (days)	pH 4.0	pH 7.0	pH 9.0
0	98	98	98
1	94	98	97
2	88	97	97
3	85	95	96
5	77	93	95
7	70	93	93
10	63	92	93
12	54	91	93
15	41	91	92
20	32	90	92

UV light (24 h) with a medium-pressure Hg lamp and sunlight (30 days, 8 h/day from May to June, 1994). The sunlight intensity of 300 to 400 nm wavelength was ~570, 1420, and 200 μW/cm² at the beginning, middle, and end of the day, respectively. Nonirradiated samples of the aqueous solution of chlorimuron-ethyl kept in darkness served as experimental controls. At various time intervals, samples were withdrawn in triplicate and analyzed by HPLC. Similarly, the rates of photolysis of chlorimuron-ethyl in pH 4.0, 7.0, and 9.0 buffered solutions were studied under UV light and sunlight. The hydrolysis study served as the dark control.

Liquid Chromatography. Chlorimuron-ethyl and its degradates in rate kinetic studies were analyzed by HPLC (waters model 400, equipped with a model 401 pump, a UV detector (240 nm), and plotter). The stationary phase consisted of a C_{18} Bondapak column (3.9 × 300 nm), and the mobile phase was methanol:water (60:40, v/v) maintained at a flow rate of 1 mL/min.

Gas Chromatography–Mass Spectroscopy (GC-MS). The GC-MS system consisted of a Shimadzu model QP-200 mass spectrometer equipped with a 50 m × 0.25 mm i.d. fused silica capillary column packed with Ulbon HR-1 (0.25 μm film thickness). The column oven temperature was programmed to increase from 100 to 250 °C in 6 min at a rate of 10 °C/min. Helium was used as a carrier gas at a flow rate of 2 mL/min.

RESULTS AND DISCUSSION

Aqueous Stability. The stability of chlorimuron-ethyl in aqueous solution was markedly influenced by pH (Table 2). At pH 4.0, hydrolysis of chlorimuron-ethyl was extensive, with an estimated half-life of 14 days. At pH 7.0 and 9.0, chlorimuron-ethyl was much more stable throughout the course of 20-day experiments than at pH 4.0. These results are similar to those reported by Brown (1990). The hydrolysis rate constant of chlorimuron-ethyl increased >150-fold as the pH drops from 7.0 to 4.0 (J. J. Dulka, personal communication, 1985).

Identification of Photoproducts. HPLC analysis of the brown residue obtained after irradiation showed the formation of eight products in addition to chlorimuron-ethyl. The degradation products were tentatively identified by GC-MS (Table 3; Figure 1). Photoproduct II was identified as benzoic acid (M^+ 122). The identification was confirmed by matching the mass spectrum of photoproduct II with that of a known standard. The mass spectrum of photoproduct III showed a molecular ion peak at m/z 150 (M^+), with fragment ion peaks at m/z 121 and m/z 105. Photoproduct III was identified as ethyl benzoate by comparison with a reference compound. Photoproduct IV was tentatively identified as 4-methoxy-2-aminopyrimidine, and its mass spectrum showed a molecular ion peak at m/z 125 (M^+). The mass spectrum of photoproduct V showed a molecular ion peak at m/z 159 (M^+). Photoproduct V was identified as 4-methoxy-6-chloro-2-aminopyrimidine. Photoproduct VI was tentatively identified as N-(4-methoxy-6-chloro-pyrimidin-2yl)-N-methyl urea, and its mass

Table 3. Mass Spectral Data of Chlorimuron-ethyl and Photolysis Products

compound	mass (m/z)
benzoic acid (II)	122 (M^+)
	105
ethyl benzoate (III)	150 (M^+)
	121
	105
4-methoxy-2-aminopyrimidine (IV)	125 (M^+)
	95
	43
4-methoxy-6-chloro-2-aminopyrimidine (V)	159 (M^+)
	129
	124
	94
	43
N-(4-methoxy-6-chloro-pyrimidin-2-yl)-N-methyl urea (VI)	217 (M^+)
	158
	129
	124
ethyl 2-aminosulfonyl benzoate (VII)	229 (M^+)
	213
	184
	121
	104
o-benzoic sulfimide (VIII) (saccharin)	183(M^+)
	119
	104
chlorimuron (IX)	386 (M^+)
	228
	184
	158
	129
	124
	104

spectrum showed a molecular ion peak at m/z 217 (M^+). Photoproduct VII was identified as ethyl 2-aminosulfonylbenzoate, and its mass spctrum showed a molecular ion peak at m/z 229 (M^+). The mass spectrum of photoproduct VIII was similar to the mass spectrum of saccharin published by Anderson and Dulka (1985). Photoproduct IX was tentatively identified as chlorimuron by its mass spectrum, which showed a molecular ion peak at m/z 386 (M^+).

The identification of these photoproducts suggests that photoreaction of chlorimuron-ethyl in water includes cleavage of the sulfonylurea bridge to give V, VII, and VIII. Photoproduct V undergoes further degradation (i.e., dechlorination) to give photoproduct IV. Photoproduct VIII is formed from the intermediate 2-aminosulfonyl benzoic acid by rearrangement. A minor photoproduct, IX, is formed by deesterifiction of chlorimuron-ethyl (Fuesler and Hanafey, 1990). Formation of ethyl benzoate (photoproduct III) would be expected as an intermediate photolysis product by analogy to the work of Weiss et al. (1980). Photoproducts V and VII are the major degradation products and photoproducts II, III, IV, VI, VIII, and IX are the minor ones.

Photodegradation Rate. The photodegradation rate of chlorimuron-ethyl was determined in distilled water, tap water, irrigation water, and buffer solutions (pH 4.0, 7.0, and 9.0) under sunlight and UV light (quartz and pyrex). The rate constant (K) was calculated by regression analysis of recovered chlorimuron-ethyl concentration versus time. The half-life ($t_{1/2}$) was calculated with the equation $t_{1/2} = 0.693/K$.

Rate of Photolysis in Buffer Solution. The photolysis rate of chlorimuron-ethyl at different buffers (pH 4.0, 7.0, and 9.0) followed first-order kinetics with significantly different rate constants and high r^2 values under both UV (quartz and Pyrex) and sunlight (Tables 4 and 5; Figures 2, 3, and 4). The photolysis rate was higher at pH 4.0 than at pH 7.0 and 9.0 (Tables 4 and
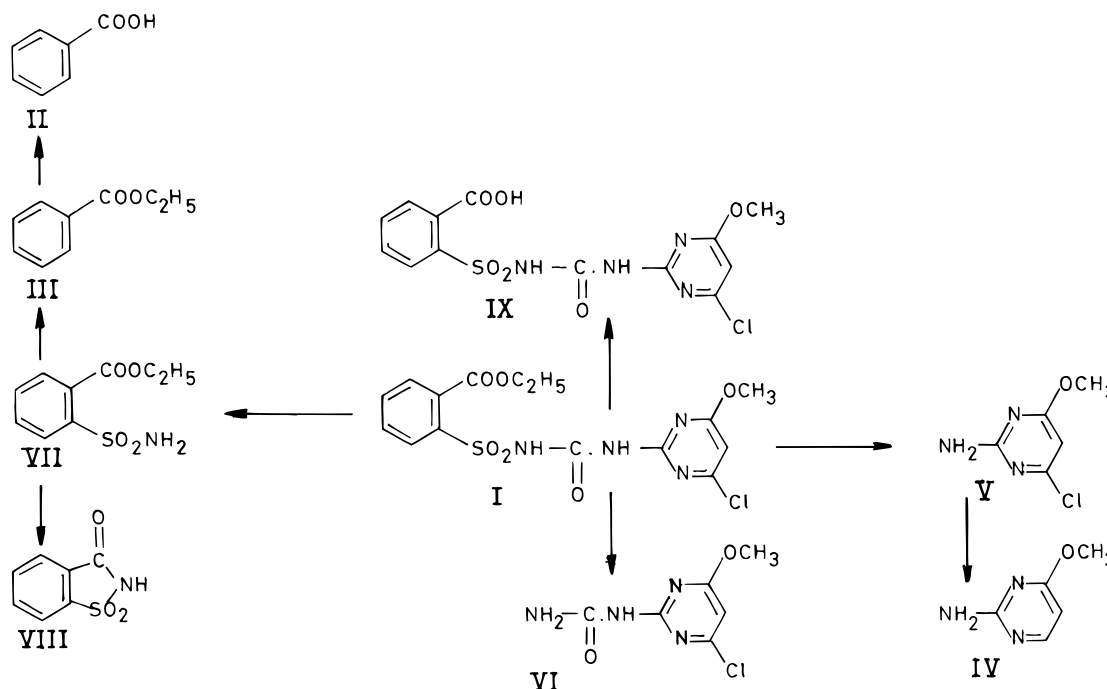
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Figure 1. Photoproducts of chlorimuron-ethyl in aqueous solution.

Table 4. Rate Constant (K) and Half-Life ($t_{1/2}$) Values for Chlorimuron-ethyl Photodegradation in Different Types of Water and pH Buffered Solutions under Ultraviolet Light

aqueous media	filter	K (h^{-1})	$t_{1/2}$ (h)	n	r^2
distilled water	Pyrex	0.0762	9.08	3	0.96
tap water	Pyrex	0.1665	4.16	3	0.95
irrigation water	Pyrex	0.2922	2.37	3	0.92
distilled water	quartz	0.0008	0.24	3	0.96
tap water	quartz	0.0019	0.1	3	0.94
irrigation water	quartz	0.0040	0.05	3	0.97
pH buffer 4.0	Pyrex	0.2072	1.25	3	0.98
pH buffer 7.0	Pyrex	0.0736	9.53	3	0.88
pH buffer 9.0	Pyrex	0.1381	5.19	3	0.98
pH buffer 4.0	quartz	0.0012	0.13	3	0.86
pH buffer 7.0	quartz	0.0045	0.25	3	0.94
pH buffer 9.0	quartz	0.0015	0.16	3	0.99

Table 5. Rate Constant (K) and Half-Life ($t_{1/2}$) Values for Chlorimuron-ethyl Photodegradation in Different Types of Water and pH Buffered Solutions under Sunlight

aqueous media	filter used	K (days^{-1})	$t_{1/2}$ (days)	n	r^2
distilled water	quartz	0.0759	9.20	3	0.96
tap water	quartz	0.1151	5.99	3	0.93
irrigation water	quartz	0.1543	4.49	3	0.97
pH buffer 4.0	quartz	0.1589	4.35	3	0.94
pH buffer 7.0	quartz	0.0736	9.53	3	0.88
pH buffer 9.0	quartz	0.0575	11.79	3	0.94

5). Interestingly, however, the rate of photolysis was higher at pH 9.0 than at 7.0 (Tables 4 and 5). These results indicate that the rate of photolysis is higher in both acidic and alkaline conditions. The rate of degradation at different pH values followed the order pH 4.0 > 9.0 > 7.0.

Photolysis Rate in Different Types of Water. The photolytic degradation rate of chlorimuron-ethyl in different types of water followed first-order kinetics with significantly different rate constants and high r^2 values (Tables 4 and 5). Degradation was more extensive in irrigation water and tap water compared with distilled water under both UV light and sunlight (Figures 2, 3, and 4). The rate of photodegradation in different types of water followed the order distilled water < tap water < irrigation water.
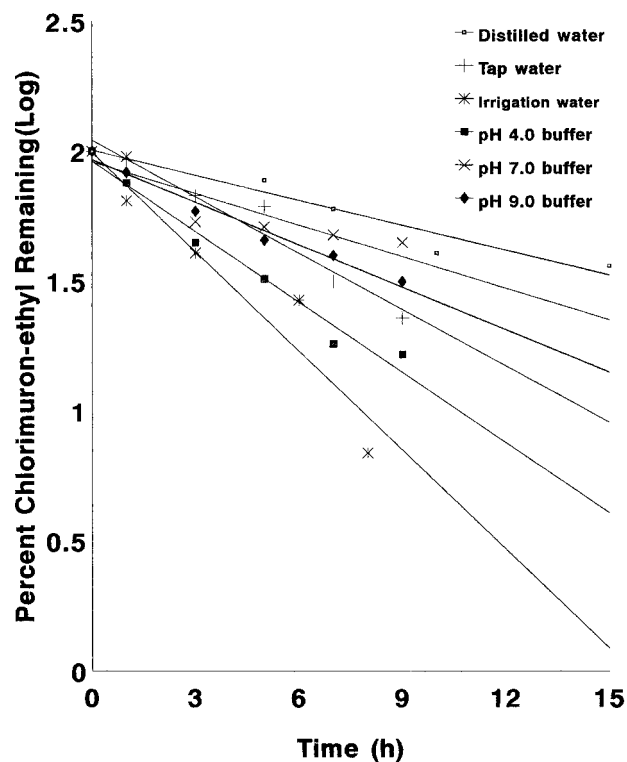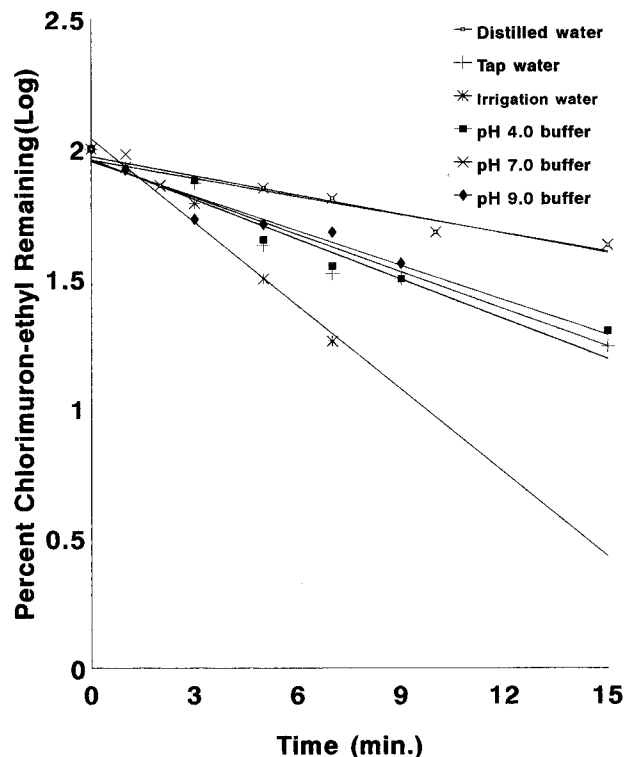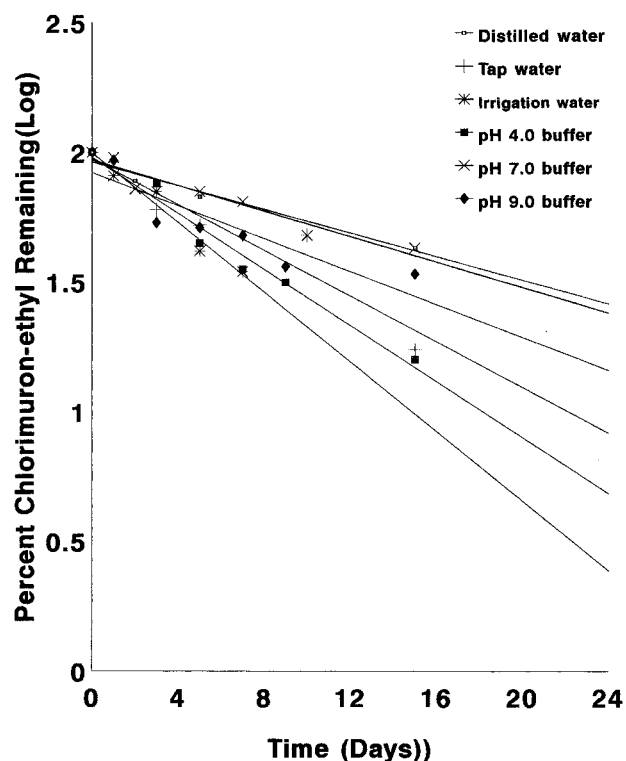

Figure 2. Photolysis of chlorimuron-ethyl in aqueous and buffer solutions with a Pyrex filter under UV light.

Three different types of water (viz., irrigation water, tap water, and distilled water) were used for this study to establish the role of dissolved inorganic substances, such as humic acid, fulvic acid, and other complex organic constituents in natural water (Draper and Crosby, 1981, 1983; Zika, 1980). Distilled water does not contain any dissolved impurities and natural sensitizers, so the rate of photolysis is lowest. In contrast, irrigation water contains dissolved inorganic substances, which may be responsible for accelerating the rate of degradation of chlorimuron-ethyl by acting as photosensitizers.

The rate of photodegradation under UV light was

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Figure 3. Photolysis of chlorimuron-ethyl in aqueous and buffer solutions with a quartz filter under UV light.

Figure 4. Photolysis of chlorimuron-ethyl in aqueous and buffer solutions with a quartz filter under sunlight.

higher when a quartz filter was used than when a Pyrex filter was used (Table 4). This difference indicates that chlorimuron-ethyl has absorption maxima that are significantly >290 nm; therefore, it undergoes photolysis more easily with a quartz filter than with a Pyrex filter. This result is supported by the absorption spectrum of chlorimuron ethyl in water, which exhibits a 213 nm band (ϵ 14 755) for the allowed $\pi-\pi^*$ transition of the phenyl ring and a 239.5 nm band, which is essentially n$-\pi^*$ in character, resulting from the lower energy band

of the aromatic ring. These $\pi-\pi^*$ and n$-\pi^*$ transitions can lead to the production of either singlet or triplet excited states responsible for photodegradation.

To determine the effect of natural conditions (temperature, air, wind), the rate of photodegradation of chlorimuron-ethyl was also studied under sunlight (Table 5). Compared with UV light, the rate of degradation under sunlight was slower, had the same pattern (Figures 2, 3, and 4), and was higher in irrigation water and in pH 4.0 buffer solutions. We conclude that natural forces did not play any role in the photolytic degradation of chlorimuron-ethyl.

Parallel control experiments in the dark with chlorimuron-ethyl in distilled water, tap water, and irrigation water showed no degradation (Figures 2, 3, and 4).

CONCLUSIONS

This study confirms and extends earlier findings that chlorimuron-ethyl is less persistent with regard to hydrolysis and photolysis in acidic conditions. Chlorimuron-ethyl photodegraded rapidly in water primarily by cleavage of the sulfonylurea bridge to give ethyl 2-aminosulfony benzoate and 4-methoxy-6-chloro-2-aminopyrimidine. Deesterification was a minor degradation pathway. The significance of this study is that photolysis of chlorimuron-ethyl was shown to obey first-order kinetics, and that the degradation half-life is concentration independent.

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