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Influence of some organic molecules on the rate and pattern of photolysis of chlorimuron-ethyl

*Partha P. Choudhury[1], Kamal K. Barman[1] and Prem Dureja[2]

[1]Directorate of Weed Science Research, Maharajpur, Jabalpur, MP,India.

[2]Division of Ag. Chemicals, Indian Agricultural Research Institute, New Delhi, India.

*Corresponding Author's E-mail: parthatinku@yahoo.com, Tel: +91 9179457045, Fax: +91 761-2353129,

ABSTRACT

Chlorimuron-ethyl, ethyl-2-(4-chloro-6-methoxy pyrimidine-2-yl-carbamoyl sulfonyl) benzoate, is a post emergence herbicide for the control of important broad-leaf weeds in soybean and maize. Though it is degraded in the agricultural environment primarily via pH-and temperature-dependent chemical hydrolysis, photolysis has also important role to degrade this compound. In this present study, the sensitizing and stabilizing effect of some organic compounds on the photolysis of chlorimuron have been investigated. The calculated half-lives of chlorimuron ethyl in presence of humic acid were 5.11 h in pyrex and 7.53 min in quartz under UV-light, and 5.78 day in quartz under sunlight, which are similar to the half-lives found in distilled water. This indicates that humic acid has no effect on the photolysis of chlorimuron in water. In another experiment, it was observed that 98 % chlorimuron was recovered in the presence of rotenone after 5 h of irradiation in pyrex tube, whereas in presence of riboflavin and benzophenone the degradation was 40.86 and 35.0%, respectively, as compared to 41.33% degradation of chlorimuron without any sensitizer. In presence of nicotine and acetone, the half-lives were 12.32 and 4.58 d, respectively, as compared to that of chlorimuron having no sensitizers in the solution (5.99 d). Thus, riboflavin and benzophenone enhance the rate of photolysis of chlorimuron whereas nicotine and rotenone significantly retard.

Keywords: Photolysis, photosensitiser, humic acid, chlorimuron ethyl

INTRODUCTION

Natural water bodies exhibit pronounced variations in composition and, consequently, in light absorption of a pesticide. These variations have important effects on dynamics and products of sunlight induced reactions of pesticides in water. The rate constants of sunlight induced reactions of a pesticide in various natural water samples can vary by order of magnitude (Simmons and Zepp 1986). This great variablity can be attributed to changes in the nature and concentration of the short-lived reactive chemical transients which are produced on the absorption of sunlight by organic and inorganic chromophores present in aquatic environments. The most important organic chromophores are humic acids, fulvic acids and humins (Choudhry 1984). Acetone, a well known triplet sensitiser, has been found to occur in

almost every natural aquatic environment (Choudhry *et al,* 1979). The irradiation of natural water samples or of solutions of humic substances provides 'solvated electrons' (Fischer *et al,* 1987; Power *et al,* 1987; Zafiriou and Bonneau, 1987; Hessler, et al. 1996 and Schmitt et al. 1995). Solvated electron, a powerful reductant, reacts rapidly with electronegative xenobiotics such as chlorinated organics as well with inorganics such as nitrous oxide and oxygen. The reaction with oxygen contributes to the formation of superoxide ion, which in part dismutes to form hydrogen peroxide, a widely distributed substance in the hydrosphere (Cooper *et al,* 1989; Draper and Crosby 1983; Petasue and Zika 1987 and Cooper and Zika 1983). The life time of hydrogen peroxide is in the range of minutes to days, which is

Table 1. Effect of humic acid on the photolysis of chlorimuron in distilled water

Nature of irradiation	Filter used	Half-life	
		Humic acid solution	Distilled water
UV-light	Pyrex	5.11 h	4.67 h
	Quartz	7.53 min	14.22 min
Sun light	Quartz	5.78 d	5.99 d

Table 2. Effect of rotenone, benzophenone and riboflavin on the photolysis of chlorimuron (Solvent: Benzene, Light: UV, Filter: Pyrex)

Time (h)	Chlorimuron remaining (%)*			
	Benzene (Control)	Rotenone	Riboflavin	Benzophenone
0	100.00	100.00	100.00	100.00
1	62.52	99.80	70.20	58.41
2	52.60	98.91	50.16	52.01
3	51.03	98.60	48.45	38.29
4	49.85	98.58	46.03	36.40
5	41.33	98.00	40.86	35.00
Half-life (h)	5.02	75.25	4.30	3.34
**r^2	0.88	0.95	0.92	0.90

*Mean of three replicates; **r: regression coefficient

Table 3. Effect of nicotine and acetone on the photolysis of chlorimuron (Solvent: water, Light: sunlight, Filter: Quartz)

Time (d)	Chlorimuron remaining (%)*		
	Water(Control)	Nicotine	Acetone
0	100.00	100.00	100.00
1	98.00	98.03	77.36
2	86.55	97.12	42.29
3	56.84	74.83	28.85
4	46.23	71.56	27.44
5	30.26	60.33	24.46
Half-life (d)	6.02	13.68	5.38
r^2	0.88	0.88	0.88

*Mean of three replicates

much longer than other transients. Its primary source in the water bodies is photochemical reactions mainly involving dissolved organic chromophores, although biota and atmosphere deposition also contribute (Cooper *et al,* 1987). Hydrogen peroxide oxidizes pesticides or forms other transients like superoxide or hydroxyl radical. The interaction between these electron-rich species and herbicide depends mainly on the chemical nature of herbicide molecules. Here, chlorimuron ethyl [(ethyl 2-(4-chloro-6-methoxy pyrimidine-2-yl-carbamoyl sulfonyl) benzoate], a sulfonyl urea herbicide was selected to get a better insight into the interaction between the sensitizers and herbicide.

Chlorimuron ethyl is a post emergence herbicide for the control of important broad leaf weeds in soybean (Worthing and Hance, 1991). It is also used as an ingredient of combination formulations for rice (Singh et al., 2008 and Saha and Rao, 2009). Though the mammalian toxicity is in the safe range (LD_{50} acute, oral,
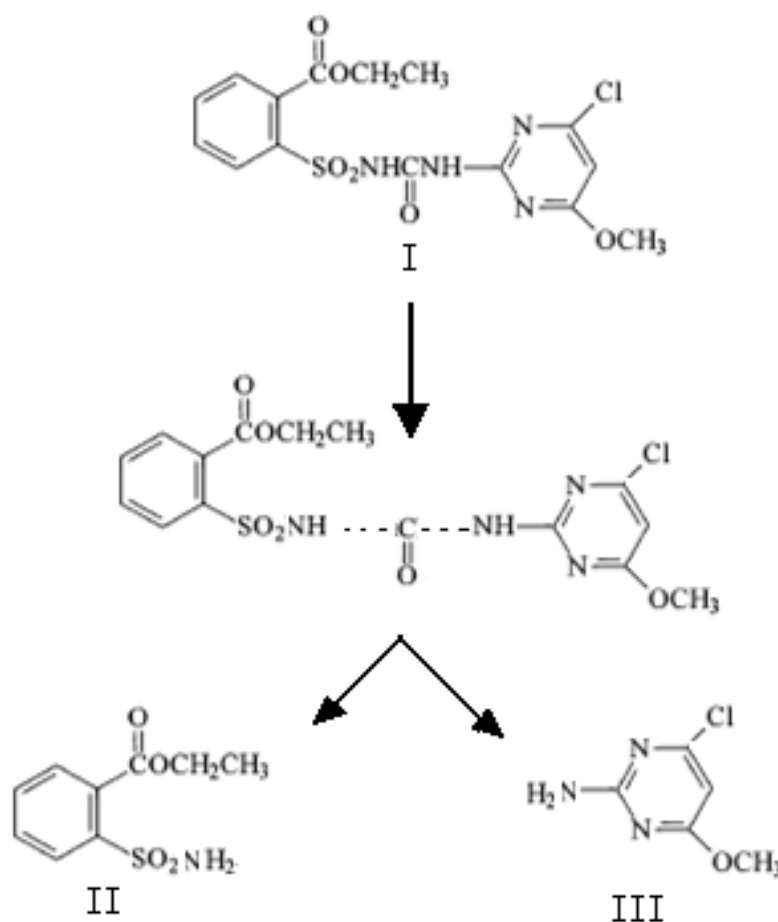
Figure 1. Photolytic cleavage of the sulfonyl urea bridge of chlorimuron ethyl

rat 4102 mgkg^{-1}), it exerts phytotoxicity to many of the succeeding crops, viz., sugar beet (Renner and Powel, 1991), corn (Curran et al. 1991), sunflower, watermelon, cucumber and mustard (Johnson and Talbert, 1993), etc. The solubility of this herbicide in water is 11mgL^{-1} (pH 5) and 1.2 gL^{-1} (pH 7) (Worthing and Hance, 1991). Albeit its persistence is moderate in soil (T$_{1/2}$ 30 days), but like many other sulfonyl urea herbicides chlorimuron's life increases with increasing pH. The half-life (T$_{1/2}$) of chlorimuron in acidic condition (pH 5) is 17-25 days, whereas in higher pH condition it may go up to 70 days (Brown, 1990 and Bedmar and coworkers, 2006). It is degraded in the agricultural environment via pH-and temperature-dependent chemical hydrolysis and is not readily susceptible to other modes of degradation (Beyer et al. 1988). Irradiation under sunlight can also degrade chlorimuron in neutral water, though slowly and the rate is faster in irrigation water probably due to the presence of dissolved organic and inorganic substances (Choudhury and Dureja 1996). The present investigation was undertaken to establish the role of some sensitisers in the photodegradation of this herbicide chlorimuron ethyl.

MATERIALS AND METHOD

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 melting point of 185^{0}C was achieved. Laboratory grade reagents and solvents were procured locally. All solvents were dried and distilled before use.

Preparation of Solution

I. Chlorimuron solution containing humic acid: 10 mL of 0.05 % humic acid was added to 190 mL of chlorimuron

solution in distilled water (approx. 40 ppm) to attain a 0.0025 % humic acid solution.

II. Chlorimuron solution containing rotenone, benzophenone and riboflavin: To a solution of chlorimuron (20 mL of 100 ppm) in benzene was added a solution of sensitizers such as rotenone, benzophenone and riboflavin (1 mL of 5 ppm)

III. Chlorimuron solution containing nicotine and acetone: To a solution of chlorimuron (10 mL of 20 ppm) in distilled water was added a solution of nicotine (1 mL of 10 ppm). Similarly, to a solution of chlorimuron (10 mL of 20 ppm) in distilled water was added acetone (0.4 mL).

Irradiation

For rate kinetic study: Solutions of chlorimuron containing humic acid, nicotine and acetone were irradiated in quartz tubes under sunlight for a period of 10 days from 8.30 am to 4.30 pm. Solutions of chlorimuron in benzene having rotenone, benzophenone and riboflavin and the solution of humic acid were irradiated in pyrex or in quartz tubes with medium pressure mercury lamp (125 W). A set of samples with all the treatments was kept in dark for 7 days. Samples were withdrawn at different time intervals, reduced to dryness and diluted to definite volume for analysis by high performance liquid chromatography.

For photoproduct isolation: Similarly, for product formation study solutions of chlorimuron ethyl were irradiated under sunlight for 5 days and under UV-light for 5 hours.

Sample preparation

After irradiation, each sample was concentrated at low temperature under vacuum. The photoproducts in the aqueous solution was partitioned into chloroform, which was then concentrated. The major photoproducts present in the concentrated solution were separated by preparative TLC (solvent system: Hexane: Acetone= 2:1). Compounds were identified by IR, NMR and mass spectra using authentic standards for comparison.

Analytical equipments

High Performance Liquid Chromatography: HPLC was carried out with a Waters Assoc. Instrument, Model 40C equipped with a pump (Model 501) and a UV detector set at 240nm. The column used was a 7μm Bondapak reversed phase column (C_{18}, 3.9X300mm); mobile phase was methanol + water (6 + 4, by volume) at a flow rate of 1.0 mL min^{-1}; volume injected was 20μL (Choudhury and Dureja, 1998).

Infrared Spectroscopy (IR): IR-spectra of photoproducts were recorded on a Nicolet Impact 700 FT-IR spectrophotometer.

Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR): ^{1}H-NMR spectra were recorded on a Bruker 400 AC spectrometer (400 MHz). Deuterochloroform ($CDCl_3$) was used as a solvent and tetramethyl silane (TMS) as the internal standard for NMR.

Mass Spectroscopy (MS): Gas chromatography-mass spectroscopy was done on a Shimadzu QP-2000 instrument. The ionization potential was 70 eV. The GC was equipped with an ULBORN HR-1 (equivalent to OV-1), fused silica capillary column (0.25 mm X 50 m, with film thickness 0.25 μm). The column oven temperature was programmed to increase from100 to 250 ^{0}C in 6 min at a rate of 10^{0}C min^{-1}. Helium was used as a carrier gas at a flow rate of 2 mL min^{-1}.

Preparation and characterization of metabolites

Acid hydrolysis of chlorimuron-ethyl: Chlorimuron-ethyl (50 mg) was dissolved in distilled water (100 mL). The pH of the solution was adjusted to 2.5 by the addition of concentrated sulfuric acid (2mL). The solution was stirred magnetically for 48h at 42 ^{0}C and then kept for 4 days at room temperature. The products formed were separated by preparative TLC, purified by crystallization from benzene and characterized by spectroscopic methods. Compounds were 4-methoxy-6-chloro-2-amino pyrimidine (III) [IR (cm^{-1}): 3460, 3323, 802; ^{1}H-NMR ($CDCl_3$) δ : 6.2 (s,1H,aromatic), 5.3(s,2H,NH_2), 3.85 (s,3H,OCH_3); Mass spectrum: 159 (M$^+$,27.7%), 129 (M$^+$ - 30), 94 (M$^+$-66,12.6%) and ethyl-2-(aminosulfonyl)benzoate (IV) [IR (cm^{-1}): 3382 3278, 2367,1723; ^{1}H-NMR ($CDCl_3$) δ : 8.15 (d,1H,Aromatic, J=7Hz), 7.85 (d,1H,Aromatic, J=5Hz), 7.65 (t,2H,Aromatic, J=5Hz), 5.84(s,2H,NH_2), 4.46 (q,2h, OCH_2CH_3, J=5Hz),1.46 (t,3H,OCH$_2$$CH_3$, J=7Hz); Mass spectrum: 229 (M$^+$,8.5%), 212 (10.6%), 184 (100%) and 121].

Results and Discussion

Chlorimuron is sufficiently stable in liquid phase at and above neutral pH. The recovery of it from all the treatment was observed at or above 92% indicating its good stability in solution. Chlorimuron ethyl absorbs UV radiation with absorption maxima at 240 and 275 nm. Even at 300 nm, it absorbs sufficient energy for the photochemical transformation. Due to its ability to absorb sufficient energy from sunlight chlorimuron undergoes direct photolysis under sunlight in aqueous phase with the half-life of around 6 days (Table-I and III). But the presence of humic acid and other organic molecules influences the photolysis of it differently. Humic acid and other humic substances, in general, sensitise photoreaction of organic molecules mostly by producing

electron rich radicals or ions. But here in this case of chlorimuron it could not alter the photolysis. A similar behavior was also observed with acetone, a well known triplet sensitiser, whereas nicotine slowed down the photoreaction ($T_{1/2}$ 13.68d) by quenching the UV-fraction of sunlight (Table-III). The effect of rotenone, benzophenone and riboflavin on the photolysis of chlorimuron was tested in benzene solution as they are insoluble in water. Riboflavin and benzophenone sensitized the reaction with the half-lives 4.3 and 3.3h, respectively, considering the half-life of 5 h in pure benzene as standard (Table-II). A similar effect of riboflavin on chlorimuron was also observed by Venkatesh et al. 1993. On the contrary rotenone allowed only 2% photolysis of chlorimuron within 5h and the half-life of chlorimuron in presence of rotenone was 75 h. Rotenone is highly photo labile and it strongly absorbs UV-light within the range of 240 to 350nm (Chen et al. 2009), which is akin to the UV-absorption range of chlorimuron ethyl. Thus it actually acted as a strong UV-screen for chlorimuron in benzene solution.

Two major photoproducts were isolated in all the treatments and characterized by spectroscopic data and authenticated by comparing with acid-hydrolysed products.

Photoproduct-1: 2-amino-4-methoxy-6-chloro-pyrimidine (III)
[IR (cm^{-1}): 3460, 3323, 802.
^{1}H-NMR (CDCl$_3$) δ : 6.2 (s,1H,aromatic), 5.3(s,2H,NH$_2$), 3.85 (s,3H,OCH$_3$).
Mass spectrum: 159 (M$^+$,27.7%), 129 (M$^+$ - OCH$_3$), 94 (M$^+$-66,12.6%).

Photoproduct-2: ethyl-2-(aminosulfonyl)benzoate (IV)
[IR (cm^{-1}): 3382 3278, 2367,1723;
^{1}H-NMR (CDCl$_3$) δ : 8.15 (d,1H,Aromatic, J=7Hz), 7.85 (d,1H,Aromatic, J=5Hz), 7.65 (t,2H,Aromatic, J=5Hz), 5.84(s,2H,NH$_2$), 4.46 (q,2h, OC$\underline{H}_2$CH$_3$, J=5Hz),1.46 (t,3H,OCH$_2$C$\underline{H}_3$, J=7Hz);
Mass spectrum: 229 (M$^+$,8.5%), 212 (10.6%), 184 (100%) and 121.

The identification of these two photoproducts suggests that the primary photoreaction of chlorimuron is the cleavage of sulfonyl urea bridge (Fig. 1). This cleavage is normally a pH dependent reaction. Generally at acidic pH the products II and III are formed, whereas above pH 7 chlorimuron is fairly stable. It is clear from the present experiment conducted in neutral solution UV radiation can also be responsible for the cleavage of sulfonyl urea bridge. In presence of riboflavin and benzophenone the cleavage is faster as they act as source of H$^+$, which sensitize the reaction. This photo cleavage has also been observed during the irradiation of chlorimuron ethyl in methanol (Choudhury and Dureja 1995), water

(Choudhury and Dureja 1996a) and on soil (Choudhury and Dureja 1996b) and leaf surface (Choudhury et al. 2007).

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