Effects of pH and Adjuvants on Clethodim Photodegradation

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Physical degradation of clethodim [2-[1-[[(3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-(ethylthio)propyl]cyclohexane-1,3-dione] occurred in aqueous solution by acid catalysis and photocatalysis in in vitro experiments as assayed by HPLC. Clethodim degradation increased as acidity increased, being further accelerated under UV light with a half-life of 2.4, 2.6, and 3.2 h at pH 5, 6, and 7, respectively. Fewer degradation products were formed under UV plus adjuvant treatments, but the rate of photodegradation was increased by 2- to 7-fold over the UV control. The degradation rate in sunlight plus adjuvant treatments was enhanced by 7- to 27-fold over the sunlight control. The photodegradation rates in the presence of adjuvants followed the sequence LI700 > Dash > Agrioil > XE1167 > CC15943 > control. In summary, clethodim degradation was catalyzed by acid, the rate being accelerated in light (probably a different mechanism), and was further enhanced by the addition of adjuvants to the light treatment.

Clethodim (Figure 1), along with other cyclohexane-1,3-dione herbicides, has excellent postemergence activity on annual and perennial grasses, but dioctyledonous plants are tolerant (Rendina and Felts, 1988). Selectivity between grasses and dicots is due to the differential response of their de novo fatty acid biosynthesis system to the herbicide (Focke and Lichtenthaler, 1987; Harwood, 1988; Kobek et al., 1988; Rendina and Felts, 1988). The specific site of inhibition is the acetyl-CoA carboxylase enzyme. In grasses, this enzyme is inhibited but the dicot enzyme is at least 400 times less sensitive (Rendina and Felts, 1988).

Previous research has shown differential clethodim performance with various adjuvants (Bridges, 1989). However, these differences cannot be accounted for on the basis of pH effects or volatilization, since clethodim volatility is quite low (Chevron Chemical Co., 1986). Differential absorption and/or physical degradation are factors that could account for the differences in activity that have been observed. Sethoxydim, another cyclohexane-1,3-dione herbicide, is known to be subject to physical degradation (Campbell and Penner, 1985; Swisher and Corbin, 1982), including photodegradation.

Therefore, the objectives of this research were (a) to identify mechanisms and rates of abiotic degradation of clethodim and (b) to determine the influence of various adjuvants on photodegradation of clethodim.

MATERIALS AND METHODS

Two series of experiments were conducted. The first series was to determine whether acid-catalyzed and/or photocatalyzed degradation of clethodim occurred and, if so, to quantify the degradation. The second series was conducted to determine the influence of various adjuvants on the rate of photodegradation of clethodim.

Mechanism and Rate of Degradation Experiments. Experimental conditions common to these studies: 50 ppm clethodim in 5 mL of 50 mM buffer solution (sodium acetate at pH 5, K_2HPO_4 at pH 6 and 7) in a glass beaker covered with a single layer of plastic film (No. 9076, Nugget Distributor, Stockton, CA) to reduce evaporation. Absorption spectra obtained on a scanning UV spectrophotometer indicated that the plastic did not interfere over the range of wavelengths of interest. For each pH, buffer stock, clethodim, and deionized distilled water were mixed and corrected for pH and then brought to volume and aliquots were made for each treatment and replicate. Beakers were shaken on a rotary shaker at 125 rpm in a growth chamber at 21 °C for the duration of each experiment.

Experiments were conducted with both technical-grade (35% active ingredient) clethodim and commercially formulated clethodim (2 lb of active ingredient/gal) to determine the influence of formulation on stability. Experiments were initially conducted in the dark to determine whether acid-catalyzed degradation occurred and to establish background data on clethodim stability. Treatments included technical and formulated clethodim at pH 5, 6, and 7. Clethodim determinations were made at 4-h intervals beginning at 0 h and continuing through 20 h.

Experiments were also conducted with artificial UV light using a bank of four 40-W Voltarc UV fluorescent tubes (Voltarc-U.S.A. FS40T12-ERE-BP) with a spectral range of 250–350 nm with peak output at 292 nm. These experiments were conducted the same as the previously described dark studies. All experiments were replicated three times and repeated.

Adjuvant Experiments. Experiments were conducted to determine the influence of five adjuvants on photodegradation of technical and formulated clethodim. The adjuvants were as follows: LI700, Loveland Industries, Greeley, CO; CC-15943 and XE-1167, Valent USA Corp., Walnut Creek, CA; Dash, BASF Corp., Parsippany, NJ; Agrioil, ChemNut Inc., Albany, GA. Experiments were conducted in artificial UV light, as previously described, and in sunlight. Sunlight experiments were conducted on Oct 7–11, 1988, at Griffin, GA, from 1100 to 1500 h. The sun's angle did not permit constant, full exposure of the solution to the rays without transmission through the glassware walls. Ambient temperature was 22 ± 1 °C.

Clethodim and adjuvant (1%, v/v) were mixed, then 100 mM K_2HPO_4 buffer (pH 7) was added, the mixture was brought to volume, and aliquots were made for treatment. Clethodim determinations were made at 0, 0.5, 1, 2, and 4 h. Clethodim solution was decanted, and the reaction vessel (Pyrex) was rinsed with an equal volume of acetonitrile and combined with the test solution. Due to physical limitations, replicates were conducted on consecutive days.

HPLC Analyses. All clethodim determinations were by HPLC at ambient laboratory temperature (ca. 22 ± 2 °C) as follows: (1) Micromeritics (Micromeritics, Inc., Norcross, GA) autoinjector 725 equipped with a 50-μL injector loop; (2) Beckman (Beckman Instrument Co., Fullerton, CA) 110A solvent delivery system operated at a flow rate of 1.0 mL/min; (3) column (250 × 4.6 mm) packed with 5-μm Hypersil C_{18} (Applied Science Labs, State College, PA); (4) Micromeritics 786 variable-wavelength detector operated at 254 nm and 0.5 AUFS; (5)

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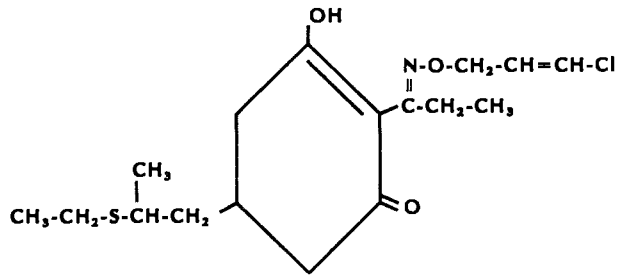

Figure 1. Chemical structure of clethodim.

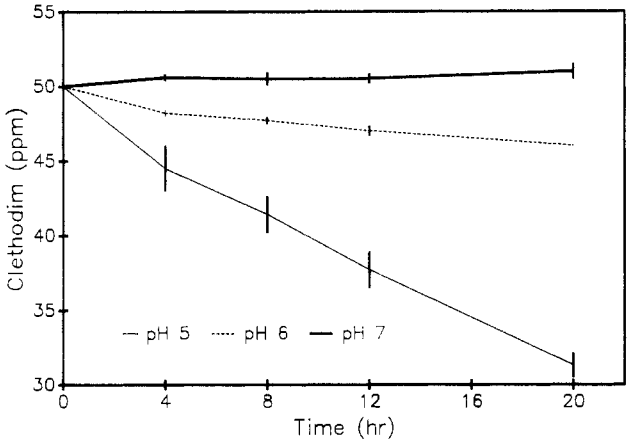

Figure 2. Technical clethodim degradation curves for pH effect in the dark. Bars represent standard error at each mean.

Hewlett-Packard 3390A integrator/recorder (Hewlett-Packard Co., Atlanta, GA) operated at a chart speed of 0.3 cm/min, threshold setting of 4, peak area rejection of 10K, signal voltage output of +0.1 → 0.4, and attenuation 10. The mobile phase, recommended by Chevron Chemical Co. (Richmond, CA), was acetonitrile–water–acetic acid (68.6:30:1.4). The acetonitrile was HPLC grade, the acetic acid was reagent grade, and the water was deionized, glass distilled, filtered through a 0.45-μm Millipore filter, and then degassed by sonication. Sample preparation was in indirect light, and samples were kept in the dark prior to injection.

RESULTS AND DISCUSSION

Mechanism and Rate of Degradation Experiments. Experiments conducted in the dark (Figure 2) show technical clethodim to be acid labile. Total recovery was obtained in the dark at pH 7, but as pH decreased, clethodim recovery decreased and total degradation products absorbing at 254 nm increased, indicating that clethodim degradation is acid-catalyzed. Clethodim degradation rates were significantly different at pH 5, 6, and 7. After 20 h, clethodim loss was 37% at pH 5, 8% at pH 6, and 0% at pH 7. Total absorbance of clethodim plus degradation products (Falb et al., 1988, unpublished data) increased with increasing pH, suggesting one or more of the following: (a) the extinction coefficient increases with pH, (b) acidic conditions result in degradation product(s) that fail to absorb at the detection wavelength of 254 nm, (c) the degradation products have very different extinction coefficients from the parent clethodim.

Under UV light, technical clethodim degradation was greatly accelerated (Figure 3) as compared to in dark conditions (Figure 2). After 20 h, the losses under UV light were 100%, 100%, and 99% in pH 5, 6, and 7, respectively. The degradation half-lives were 2.4, 2.6, and 3.2 h at the respective pHs and were significantly different at pH 5, 6, and 7. The differences among pHs in UV light can be accounted for by acid degradation, since at

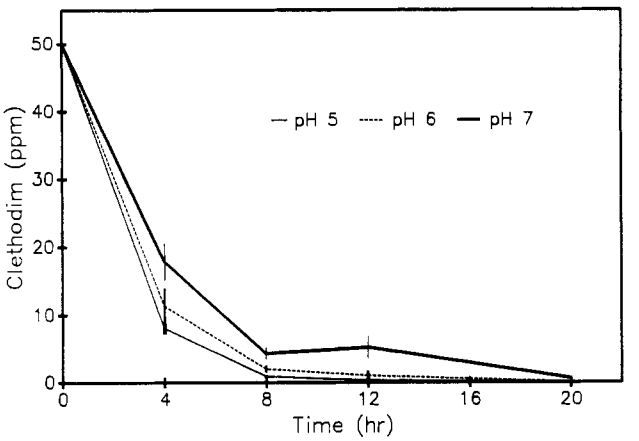

Figure 3. Technical clethodim degradation curves for pH effect under UV light.

neutrality only photodegradation occurred, as expected on the basis of data in Figure 2. As pH decreased, acid catalysis increased but light was still the major component of degradation. The HPLC system separated 9 products under dark conditions and 13 under photodegradation conditions (Table I), four of them being unique to light conditions. It is probable that the degradation mechanisms differ in acid catalysis and photocatalysis.

Degradation rates with two EC commercially formulated clethodim (Figures 4 and5) were very similar to the rates for technical clethodim, including similar half-lives. However, the formulated clethodim (Figure 4) showed slightly less degradation at pH 5 and 6 compared to technical clethodim (Figure 2). The primary difference was the lack of acid (dark) degradation at pH 6. Thus, the commercial formulation slightly improved the stability of clethodim. The degradation products appeared to be similar compounds, based on relative retention times (RRTs). Thus, degradation of technical-grade and commercially formulated clethodim was similar quantitatively and qualitatively under the pH and UV light conditions tested.

Adjuvant Experiments. The addition of adjuvant to clethodim is required to obtain consistent herbicidal performance in the field. Therefore, the effect on photodegradation of adding adjuvant to clethodim was also studied. UV degradation of clethodim was considerably increased by the inclusion of various adjuvants (Figure 6). The half-lives were 0.4 h (LI700), 0.5 h (Dash), 0.8 h (XE-1167), 0.9 h (Agrioil), 1.4 h (CC-15943), and 3.0 h (zero adjuvant control) at pH 7 and 1% adjuvant concentration. The relative rates of photodegradation were statistically significant in the following order: LI700 = Dash > XE1167 = Agrioil > CC15943 > control. It can be assumed that only the 30-min and 1-h data in Figure 6 are biologically relevant because if clethodim is not absorbed into the leaf or epicuticular wax within 1 h, it will probably precipitate on the leaf surface following solvent evaporation.

A total of eight different products were formed in the adjuvant solutions under UV light, and five of the products appear to have a similar RRT to those discussed in the previous experiments (Table I). The three most common products generally showed a similar trend over the time course. Thus, fewer UV degradation products are formed in the presence of adjuvants, but the rate of photodegradation is increased by 2- to 7-fold.

Photodegradation under sunlight (Figure 7) was comparable to that under UV. The half-lives were 0.3 h (LI700), 0.4 h (Dash), 0.7 h (Agrioil), 0.8 h (XE-1167),

Table I. Relative Retention Times (RRT) of Peaks Eluted from the HPLC Column

figure	treatment	pH	RRT[a] 0.18	0.20	0.21	0.22	0.24	0.25	0.28	0.31	0.32	0.37	0.41	0.58	0.68	0.74	0.83	1.07
2	technical clethodim, dark	5	+							+	+	+	+			+		
		6	+	+				+		+	+	+				+		+
		7	+	+				+		+	+	+				+		+
3	technical clethodim, UV	5	+				+		+	+	+	+	+		+	+		+
		6	+	+		+	+	+	+	+	+	+	+		+	+		+
		7	+	+		+	+	+	+	+	+	+	+		+	+		+
4	formulated clethodim, dark	5	+					+	+	+	+	+	+		+	+		
		6	+	+				+		+	+	+			+	+		+
		7	+	+				+		+	+	+			+	+		+
5	formulated clethodim, UV	5	+	+			+	+	+	+	+	+	+		+	+		+
		6	+	+			+	+	+	+	+	+	+		+	+		+
		7	+	+			+	+	+	+	+	+	+		+	+		+
6	UV control	7			+						+	+	+					
	CC15943	7			+					+	+	+						
	XE1167	7			+					+	+	+						•
	Agrioil	7			+						+	+	+				+	+
	Dash	7			+						+	+	+	+				+
	L1700	7			+						+	+	+	+			+	
7	sun control	7			+	+	+		+	+	+	+				+		+
	CC15943	7			+	+	+		+	+	+	+		+		+	+	
	XE1167	7			+	+	+		+	+	+	+				+	+	+
	Agrioil	7			+	+	+		+	+	+	+		+		+	+	
	Dash	7			+	+	+		+	+	+	+		+		+		+
	L1700	7			+	+	+		+	+	+	+		+		+	+	+

[a] RRT are based on the parent clethodim as the internal standard.

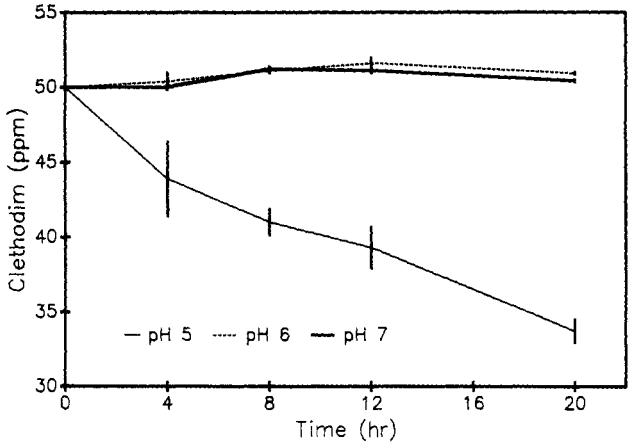

Figure 4. Formulated clethodim degradation curves for pH effect in the dark.

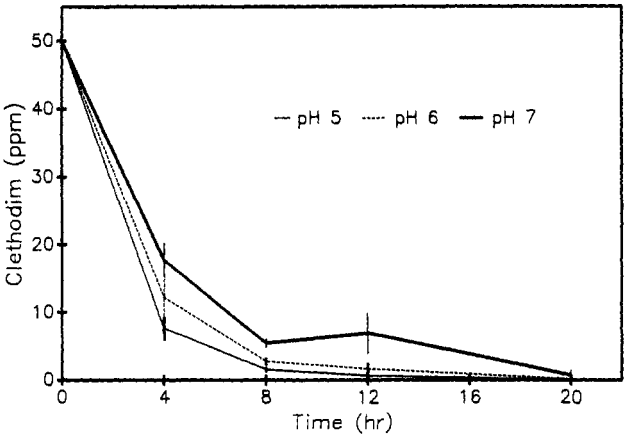

Figure 5. Formulated clethodim degradation curves for pH effect under UV light.

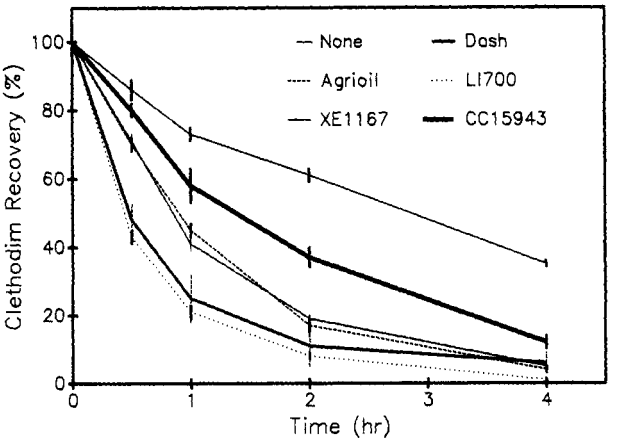

Figure 6. Formulated clethodim degradation curves under UV light and containing 1% adjuvant concentration.

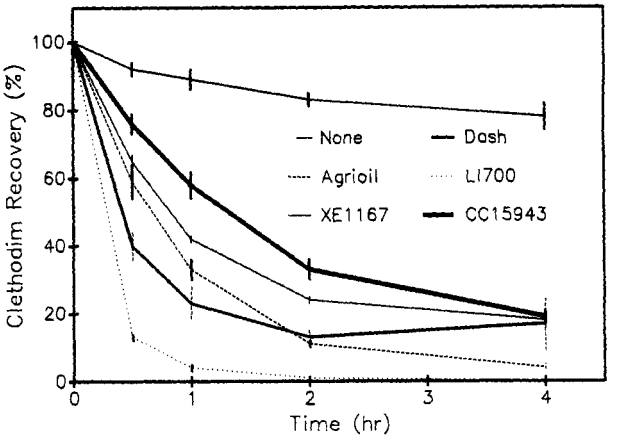

Figure 7. Formulated clethodim degradation curves in sunlight and containing 1% adjuvant concentration.

and 1.3 h (CC-15943). The control (clethodim without adjuvant) never reached 50% degradation; extrapolation suggests a half-life in excess of 8 h. Therefore, photodegradation trends among adjuvants were similar in the two light regimes, but catalysis was slightly faster under sunlight except the control, which was much slower. Apparently, the effectiveness of clethodim photodegradation was much higher in sunlight. The UV light source had an emission range of 250–350 nm whereas the UV cutoff of sunlight is around 290 nm (Crosby, 1976). There-

Table II. Effect on Absorbance Readings ($\times 10^6$)[a] of Adding Acetonitrile to Adjuvant Stock Solutions

treatment	stock	stock + acetonitrile
control	122	66
CC15943	105	64
Agrioil	104	65
XE1167	88	62
Dash	59	68
L1700	43	56

[a] Readings are the HPLC detector response (in millions) based on absorbance at 254 nm. The stock contained 100 mM potassium phosphate (pH 7) and 50 ppm clethodim. Treatments in the right-hand column contained an equal volume of acetonitrile added to the stock. Adjuvant concentrations were 1%.

fore, the long-wave UV and/or blue-violet light may be more effective in catalyzing clethodim photodegradation in the presence of these adjuvants.

The relative rates of photodegradation under sunlight were statistically significant in the following order: LI700 > Dash > Agrioil > XE1167 > CC15943 > control. As in Figure 6, only the data at 30 min and 1 h are considered biologically relevant in Figure 7. Exposure of aqueous clethodim–adjuvant solution to sunlight for only 30 min resulted in losses ranging from 24% with CC15943 to 87% with LI700. A total of 11 different products (based on RRTs) were formed in the sunlight plus adjuvant treatments while the control had 9 products and each adjuvant solution had 10 or 11 products. The 5 most prevalent products showed a similar trend over the time course. LI700 and Dash photoproducts showed some distinction from the other treatments when product formation trends are compared over time. The rate of degradation in sunlight was increased with addition of adjuvants by 7- to 27-fold over the control. More photoproducts were formed in sunlight, even in the controls, than under UV. The experimental methods allowed for detection of only those products that absorbed light at 254 nm.

Two interesting phenomena were observed: unexpected UV absorption changes during dilution of the adjuvant stock solutions and comparison of these absorbance changes with the half-life of the adjuvant solutions. The original stock solutions (100 mM phosphate buffer, pH 7) varied more than 2-fold in absorbance (Table II) despite having the same concentrations of clethodim and being well within the linear absorbance range of the control. After addition of an equal quantity of acetonitrile, only the control had the expected 50% decrease in absorbance. All of the adjuvant solutions had absorbances greater than 50%, and two of them even had a higher reading after being diluted. We interpret this to be the result of the lipophilic clethodim molecules forming aggregates (micelles) within the aqueous continuous phase, resulting in violation of the Beer–Lambert law. Addition of acetonitrile greatly reduced the variability betwen solutions (Table II), presumably due to the disruption of aggregates, which permitted the lipophilic clethodim molecules to act independently of each other. Adequate controls were utilized in these experiments; thus, the results reported herein were not influenced.

The rate of clethodim photodegradation in the adjuvant solutions (Figures 6 and 7) is inversely related to the absorbance readings of the stock solutions (Table II). This further supports the hypothesis given above. Apparently, not only does acetonitrile cause micellar dissociation so that the clethodim molecules act independently, resulting in a uniform UV absorption response, but this dilution would also decrease clethodim photodegradation by decreasing the chain reactions between clethodim molecules whether the degradation mechanism is by free-radical formation or energy transfer.

The abiotic transformations of clethodim have much in common with sethoxydim, another herbicide in the cyclohexanedione class. Sethoxydim also undergoes decomposition in aqueous solutions, is acid-labile, and is subject to rapid UV degradation (Campbell and Penner, 1985; Shoaf and Carlson, 1986, and references therein). However, there are conflicting data on the effect of pH (Shoaf and Carlson, 1986). Sethoxydim appears to form a large number of photoproducts, perhaps as many as 10 or 12 (Campbell and Penner, 1985; Shoaf and Carlson, 1986) degradation products.

We are continuing our investigation on the characterization of the degradation products and reaction mechanisms.

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Registry No. LI700, 120528-51-0; CC15943, 125249-36-7; XE-1167, 125249-39-0; Dash, 118548-23-5; Agrioil, 125249-35-6; clethodim, 99129-21-2.