

## Picloram Photolytic Decomposition

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Picloram (4-amino-3,5,6-trichloropicolinic acid), as the sodium salt in aqueous solution, readily decomposed when irradiated with ultraviolet light (300–380 nm). During photolysis, two chloride ions were produced per molecule of picloram

photolyzed. Evidence was obtained to suggest that both a free radical and an ionic mechanism are involved in the photolysis of picloram. The overall reaction proceeds by a nonchain mechanism.

The persistence of the chlorinated herbicide 4-amino-3,5,6-trichloropicolinic acid (picloram) in soil has been shown to vary greatly (Goring *et al.*, 1965; Herr *et al.*, 1966). Soil texture, moisture, and temperature affect the persistence of this compound (Merkle *et al.*, 1967). Another factor which should have an effect on the persistence of picloram is sunlight. Picloram weakly absorbs light in the 290–340-nm portion of the ultraviolet region of the spectrum (Zweig, 1967). Absorption in this region is significant, as the sun's ultraviolet radiation which reaches the earth's surface essentially ends at 290 nm (Gates, 1959). The degradation of picloram by ultraviolet light (254 nm) has been shown (Hall *et al.*, 1968). Hedlund and Youngson (1972) have shown that picloram exhibits pseudo-first-order kinetics when photolyzed by sunlight. In this report the extent of decomposition of picloram in aqueous solution is discussed, reaction products are quantitated, and mechanistic possibilities are suggested.

### EXPERIMENTAL SECTION

**Irradiation Chamber.** The picloram solutions were irradiated in cylindrical quartz cells (30 ml, 10 cm × 2 cm diameter) by uv light, 300–380 nm, with maximum intensity at 366 nm. The four-coated, 15-W, low-pressure mercury vapor lamps were made by General Electric (No. F15T8). A holder was fixed to the bottom of the irradiation chamber to maintain exactly 11 cm from the four lamps, and the temperature of the chamber was maintained at 30° (Mosier *et al.*, 1969).

**Picloram Solutions.** The Dow Chemical Co. furnished the 99% pure nonlabeled picloram and the [<sup>14</sup>C]carboxyl carbon-labeled picloram (4.14 μCi/mg). All solutions used for irradiation were prepared as the sodium salt of picloram in aqueous solution ( $2.08 \times 10^{-3}$  M). One liter of standard solution was prepared by adding 490 mg of nonlabeled and 10 mg of <sup>14</sup>C-labeled picloram to water and adjusting the pH to 9.5. Following irradiation, the entire 30-ml sample was acidified to pH 2, evaporated to dryness under vacuum, and taken up in methanol. The methanol solution was methylated by diazomethane produced from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide by a procedure described by Schlenk and Gellerman (1960) and concentrated to 2 ml by a stream of dry air.

**Thin-Layer Chromatography (tlc).** Glass plates (20 × 20 cm) were coated with a 0.25-mm layer of Adsorbosil-1 (silica gel) and activated for 30 min at 130°. The developing solvents were (I) benzene-methanol-acetic acid (25:4:1) and (II) benzene-acetic acid (15:2:48). Twenty microliters of the 2-ml concentrate was applied to 0.25-mm plates for subsequent radioactivity measurements of degradation products. For uv analysis, a 200-μl aliquot was applied to 2-mm thick tlc plates to obtain sufficient amounts of materials. The appropriate sections were removed from the plates, extracted with ethanol, and concentrated under a stream of dry air. Thin-layer plates

were sprayed with Rhodamine B (0.5 mg/10 ml of ethanol) and viewed under ultraviolet light.

**Scintillation Counting.** The irradiated solutions were spotted and chromatographed two-directionally by the above method, which is described in detail by Guenzi and Beard (1967). Plates were sprayed with Rhodamine B and placed under ultraviolet light, dark-colored products outlined, and the spots removed by vacuum directly into a scintillation counting vial containing a counting solution composed of 4 g of PPO (2,5-diphenyloxazole) and 50 mg of POPOP (*p*-bis-(2,5-phenyloxazolyl)benzene) in 1 l. of toluene. Radioactivity was measured with a liquid scintillation counter.

**Gas Chromatography.** The instruments used were Beckman models GC-4 and GC-5 equipped with electron capture detectors. A 1.8-m borosilicate glass column (6 mm o.d., 4 mm i.d.) was packed with equal portions of 10% Dow-Corning 200 silicone fluid and 15% QF-1 by weight on 80/100 mesh Gas Chrom Q. Operating conditions of the chromatograph were: inlet temperature, 235°; column, 220°; detector, 270°; and carrier gas (He) flow, 100 ml/min. Following methylation, irradiated samples were analyzed by gc for possible products, which included 4-amino, 2,3,5-trichloropyridine, and 4-amino-3,5-dichloro-6-hydroxypicolinic acid. Quantitation of the parent compound by gc was conducted to confirm the radioactivity measurements.

**Chloride Analysis.** Chloride ion production was determined by potentiometric titration with silver nitrate solution using a glass silver-silver chloride electrode system (American Public Health Association, 1965).

**Quantum Yield.** Quantum yield determinations were made using the potassium ferrioxalate actinometer method as described by Parker (1953) and Hatchard and Parker (1956).

**Salt Solution.** To determine the effect of ionic strength on picloram photolysis, salt was added to an aqueous picloram solution ( $2.08 \times 10^{-3}$  M) to give three concentrations of NaCl ( $2.0 \times 10^{-3}$ ,  $2.0 \times 10^{-2}$ , and  $2.0 \times 10^{-1}$  M) in the reaction mixture.

### RESULTS AND DISCUSSION

Irradiation of a  $2.08 \times 10^{-3}$  M aqueous solution of the picloram sodium salt with 300–380 nm uv light resulted in 99% degradation of the parent compound within 72 hr (Table I). After 5, 15, 25, 34, and 48 hr of irradiation, the amounts of picloram degradation were 15, 27, 31, 61, and 90%, respectively (all picloram solutions were analyzed as the methyl ester, solutions were methylated by diazomethane). After 34 hr of irradiation, 11 visually observable degradation products, excluding the spot of origin (spot no. 1) and parent compound (spot no. 13), were separated by tlc (Figure 1). Eight of these spots had radioactivity above background, which indicated that the carboxyl carbon (<sup>14</sup>C) was still intact. No radioactivity was detected in the other three compounds, spots 5, 6, and 8, indicating decarboxylation.

The changes in product formation with increased length of irradiation (Table I) suggest that more than one photo-

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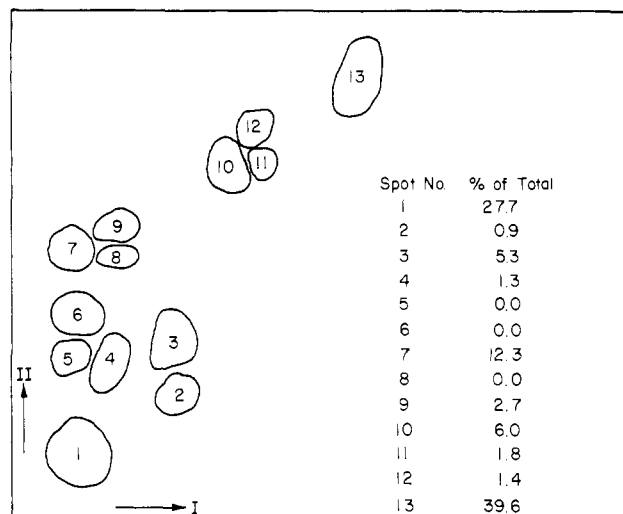
**Table I. Thin-Layer Separation and Quantitation of Photolyzed Picloram Decomposition**

Spot no. <sup>a</sup>	Length of irradiation, hr					
	5	15	25	34	48	72
	% of total activity spotted					
1	2.0	2.7	2.7	27.7	52.7	59.33
2	7.69 <sup>b</sup>	17.51 <sup>b</sup>	11.14 <sup>b</sup>	0.9	0.4	c
3				5.3	1.8	c
4	2.26	0.76	8.58	1.3	0.6	c
5	c	c	0.36	0.0	0.0	1.4
6	c	c	c	0.0	0.0	1.0
7	c	c	c	12.3	24.1	34.3
8	c	c	c	0.0	0.0	c
9	c	c	0.5	2.7	6.2	2.7
10	1.8 <sup>d</sup>	3.85 <sup>d</sup>	6.50	6.0	3.7 <sup>d</sup>	c
11			c	1.8		c
12			c	1.4		c
13	85.4	73.3	69.3	39.6	10.0	1.4

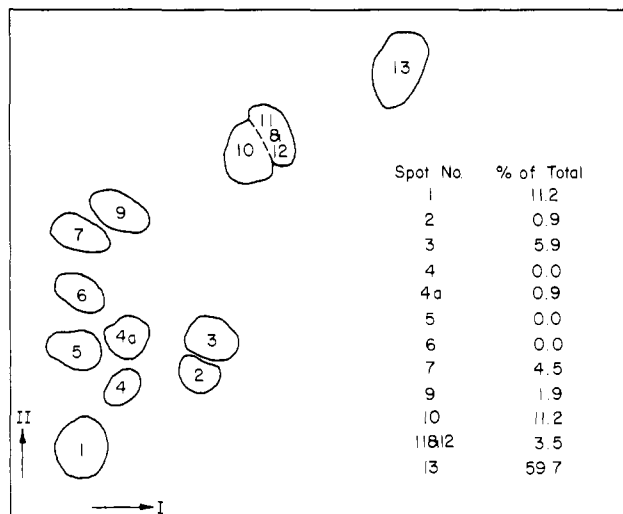
<sup>a</sup> All spot numbers are in reference to Figure 1. These data are most meaningful if Figure 1 is observed in conjunction with this table. <sup>b</sup> Spots 2 and 3 are combined. <sup>c</sup> No spot was observed. <sup>d</sup> Spots 10, 11, and 12 are combined.

chemical pathway occurs. Products which are observed on spots indicated as 2 and 3 are initially formed (2 and 3 were not always completely resolved by tlc, thus are reported as one), with the maximum amount at 15 hr. These compounds are probably further photolyzed to polymers which do not move on tlc and remain at the origin (spot no. 1). After 34 hr of irradiation, spot no. 7 begins to accumulate, and this accumulation continues up to the 72-hr period. Evaluation of these data suggests that these two compounds or groups of compounds are formed by different mechanisms. Unfortunately, the numerous attempts at separation and characterization of these compounds were unsuccessful. However, more information was obtained on functional groups and the existence of the intact ring structure. Ultraviolet analyses of products corresponding to spots 3, 7, and 10 separated by tlc (Table I, Figure 1) showed that the ring remained intact. The uv absorption maxima were 295, 300, and 300 nm for spots 3, 7, and 10, respectively, and 310 nm for picloram methyl ester. The activity in each of these tlc spots (Figure 1) and an nmr peak corresponding to three protons of picloram methyl ester group at  $\delta$  1.9 indicated that the carboxyl group remains on the ring. The presence of the  $-\text{NH}_2$  in each fraction was confirmed by an nmr peak at  $\delta$  6.2 corresponding to two protons. Irradiated picloram samples (15, 34, and 48 hr) were cochromatographed by glc and tlc with 4-amino-3,5-dichloro-6-hydroxypicolinic acid and 4-amino-2,3,5-trichloropyridine, and none of the irradiation products corresponded to either of these two compounds. The photolysis results of 6-chloropicolinic acid by Redemann and Youngson (1968) may explain why the 4-amino-3,5-dichloro-6-hydroxypicolinic acid was not found in our studies. Their studies showed that the photolysis of 6-chloropicolinic acid proceeds by the dechlorination and formation of 6-hydroxypicolinic acid. The decomposition of the hydroxy compound was faster than the dechlorination step, and therefore no buildup of hydroxy product was found in the reaction mixtures.

To determine the effect of dissolved oxygen in the photolysis solutions, nitrogen was continuously bubbled through the reaction cylinder at a rate of 3 ml/min during the photolysis period (photolysis and gas flow were begun simultaneously, which resulted in a system reduced in oxygen content but not oxygen free). The gases that came out of the cell were passed through consecutive traps of toluene, dioxane, and 1 N KOH. Less than 0.1% of the total radioactivity was trapped in the two organic solvent



**Figure 1.** Separation of a 34-hr irradiated solution of picloram and its degradation products on a two-directional thin-layer chromatogram. Values were obtained from radioactivity measurements of individual spots. Number 13 is the methyl ester of picloram. Solvent I: benzene-methanol-acetic acid (25:4:1). Solvent II: benzene-acetic acid (152:48).



**Figure 2.** Separation of a picloram solution with  $\text{N}_2$  continuously being bubbled during the 34-hr irradiation period and its degradation products on a two-directional thin-layer chromatogram. Values were obtained from radioactivity measurements of individual spots. Number 13 is the methyl ester of picloram. Solvent I: benzene-methanol-acetic acid (25:4:1). Solvent II: benzene-acetic acid (152:48).

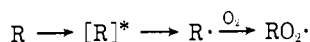
traps, while 1.7% of the total  $^{14}\text{C}$  added could be accounted for as  $^{14}\text{CO}_2$ . These results indicated that some decarboxylation occurred, and if any ring fission occurred, the carboxyl portion of the fragment is not volatilized. In this system the reaction rate was decreased and the concentration of the normally observed products was altered (Figure 2). Comparison of the irradiated products with and without nitrogen gas present (Figures 1 and 2) indicated that with nitrogen present: (a) only one-half as much material remained at the origin; (b) spot no. 7 was reduced by 63% and the activity in spot no. 10 was increased by 50%; and (c) the concentration of the parent compound (spot no. 13) was 1.51 times greater. The increased photolytic rate observed in the presence of oxygen may have resulted from the reaction of oxygen, with the proposed picloram-free radical formed in the primary photolytic process. The primary reaction between a free radical  $\text{R}\cdot$  at ordinary temperatures, according to Calvert and Pitts (1966), is

Table II. Effect of N<sub>2</sub> and NaCl on the Photolysis of Picloram

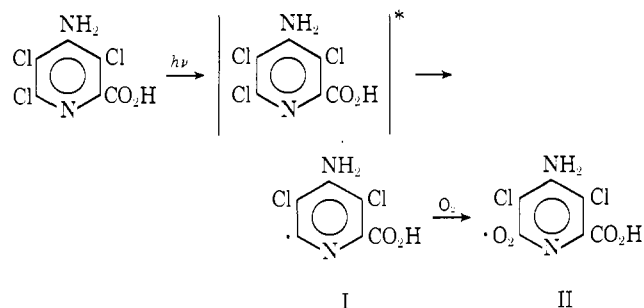
Irradiation period, hr	Material added	Concentration, M	Picloram decomposed, %
25	None		30.7
25	NaCl	$2.0 \times 10^{-3}$	56.3
25	NaCl	$2.0 \times 10^{-2}$	45.0
25	NaCl	$2.0 \times 10^{-1}$	44.7
34	None		60.5
34	N <sub>2</sub> <sup>a</sup>		40.3

<sup>a</sup> N<sub>2</sub> gas bubbled through the reaction tube at a rate of 3 ml/min during irradiation.

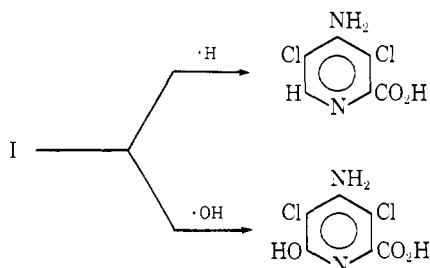
described by:



A possible sequence of events for photolysis is as follows.



The proposed radical intermediate I may abstract H and/or OH from the solvent to form the following possible products, which are rapidly decomposed.

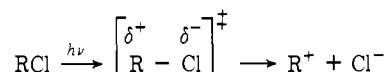


According to Redemann and Youngson (1968), who studied the photolysis of 6-chloropicolinic acid, 6-hydroxypicolinic acid was the initial photoproduct and was photolyzed more rapidly than the parent compound. As a result, in a study where they used direct sunlight, the hydroxy compound was not detected as the photolysis product of 6-chloropicolinic acid. This may have been the case in our study where 4-amino-3,5-dichloro-6-hydroxypicolinic acid was never detected.

The pH of the basic initial reaction solution (9.5) decreased to 6.0 after 34 hr of irradiation. This decrease indicated that an acid or acids was/were being formed from picloram during photolysis. As HCl was thought to be a likely product, irradiated solutions were analyzed for chloride content. The ratio of chloride ions produced to the number of picloram atoms decomposed for 15, 25, and 34 hr of irradiation was 1.6, 1.8, and 1.9, respectively. These results agree with Hall *et al.* (1968) in that for each molecule of picloram degraded, two chloride ions are produced.

Since chloride ions are produced during the photolytic process, it was thought that the addition of chloride ions, as NaCl, to picloram solutions should influence the reaction. According to Gould (1959), reactions in which ionic charge is created from neutral molecules exhibit faster reaction rates as ionic strength increases. If the photolysis

of picloram involves ion production in a rate-determining step, then increasing the ionic strength should increase the rate of decomposition. Such an increase in reaction rate was observed when picloram solutions containing  $2.0 \times 10^{-3}$  M,  $2.0 \times 10^{-2}$  M, and  $2.0 \times 10^{-1}$  M NaCl were photolyzed (Table II). The ionic strengths of the picloram solutions with no added NaCl were 0.0045 (because of the NaOH added to adjust the pH to 9.5), 0.0065, 0.0245, and 0.2045 with salt additions, respectively. The increased photolytic rate due to salt additions may be a result of driving the following reaction toward ionic products (Gould, 1959):



Photolytic decomposition of picloram in aqueous solution appears to be a combination of both an ionic and free radical process. The decomposition from each process was shown by varying O<sub>2</sub> for the free radical process and by varying salt concentration for the ionic process. Thus, the contribution of each mechanism on total decomposition would be dependent on variables that would influence both ionic and free radical reactions.

Quantum yield determinations by the potassium ferrioxalate actinometer method (Hatchard and Parker, 1956; Parker, 1953) yielded a value of 0.005, which indicates that the process is not a chain reaction and that the overall efficiency of the photolytic process is low. The quantum yield could be slightly higher than 0.005 due to possible absorption by photoproducts formed during the photolysis reaction.

The photolysis of picloram under a variety of conditions suggests a complex, nonchain process involving both free radical and ionic mechanisms. The principal free radical products are probably oxidation products, while the products of the ionic mechanism are not known. The limited <sup>14</sup>C<sub>2</sub>O<sub>2</sub> production indicates that decarboxylation is not the major degradation pathway.

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