

4-CPA shown in Figure 4. However, the close analogy between these products and those obtained from the photolysis of 2,4-D (Crosby and Tutass, 1966) and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) (Crosby and Wong, 1973) indicates that the pathway will be general for the other commercial phenoxy herbicides.

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## Photodecomposition of 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) in Water

Donald G. Crosby\* and Anthony S. Wong

Photodecomposition of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in aqueous solution principally involved cleavage of the ether bond and replacement of the ring chlorines by hydroxyl and by hydrogen. The major products were 2,4,5-trichlorophenol and 2-hydroxy-4,5-dichlorophenoxyacetic acid; 4,6-dichlororesorcinol, 4-chlororesorcinol, 2,5-dichlorophenol, and a dark polymeric product also were isolated. The

toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was not detected among the photodecomposition products. 2,4,5-T photolyzed very slowly compared to its 4-chloro and 2,4-dichloro analogs, but the 11-fold increase in photolysis rate caused by sensitization with acetone or riboflavin suggests that sunlight can be an important factor in the environmental degradation of 2,4,5-T.

For almost three decades, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, I) and its derivatives have received wide use as herbicides, especially for control of brush, jungle, and aquatic weeds. For example, the 1968 U. S. production of these compounds exceeded 60 million pounds (U. S. Tariff Commission, 1970), and residues have been detected in crops, soil, the atmosphere (Barnesberger and Adams, 1966), rainwater (Cohen and Pinkerton, 1966), and surface waters (Thoman and Nicholson, 1963). The fate and persistence of 2,4,5-T in the environment have been the subject of considerable investigation (Loos, 1969; PSAC, 1971); this report deals with the influence of sunlight, natural and simulated, on aqueous solutions of 2,4,5-T and its salts.

#### EXPERIMENTAL SECTION

**Materials.** 2,4,5-T, 2,4,5-trichlorophenol (II), 4,6-dichlororesorcinol (III), 2,5-dichlorophenol (IV), and 4-chlororesorcinol (V) were purified commercial products. 2,4,5-T was recrystallized three times from benzene, mp 153.5–54.5°. The trichlorophenol was freed of persistent impurities by dissolving it in aqueous sodium hydroxide solution, extracting neutral impurities with several portions of benzene, acidification, recrystallization three times from benzene, and sublimation under reduced pressure, mp 67.5°.

**Irradiation.** Solutions of 2,4,5-T (100 mg/l.) in distilled water were adjusted to pH 8 with 0.1 *N* sodium hydroxide and irradiated outdoors with summer sunlight in Davis, Calif., or indoors with ultraviolet (uv) light in the wavelength region of 300–450 nm. The irradiations were conducted in 3-l. borosilicate glass flasks, those indoors mounted in a 14 in. (i.d.) × 5 ft cylindrical chamber (Figure 1) constructed of Transite pipe cut in halves longitudinally, hinged, and lined with bright aluminum sheet. The chamber was fitted with six 4-ft F40BL fluorescent uv lamps (Crosby and Tang, 1969), three clamped to the fixed half and three to the hinged door. Light intensity measured with a YSI radiometer (Yellow-Springs Instrument Co., Yellow Springs, Ohio) was 390  $\mu\text{W}/\text{cm}^2$  at the center of the chamber and 785  $\mu\text{W}/\text{cm}^2$  halfway from the center to the lamp surface. The chamber temperature remained close to 30°, and filtered air was passed through the solutions to maintain oxygen saturation and efficient agitation. The removable hood and vent for toxic compounds were not used in the present experiments.

The indoor irradiation was allowed to proceed for 200 hr, and 50-ml aliquots were withdrawn at intervals and analyzed by gas-liquid chromatography (glc). Equivalent experiments were conducted with: (A) 2,4,5-T in 0.5% aqueous sodium bisulfite; (B) aqueous 4-chlorophenoxyacetic acid (4-CPA) at pH 8; and (C) aqueous 2,4-dichlorophenoxyacetic acid (2,4-D) at pH 8, as well as in the dark. The exposure time for the outdoor preparative scale experiments amounted to about 9 hr each day for 60 days (540 hr).

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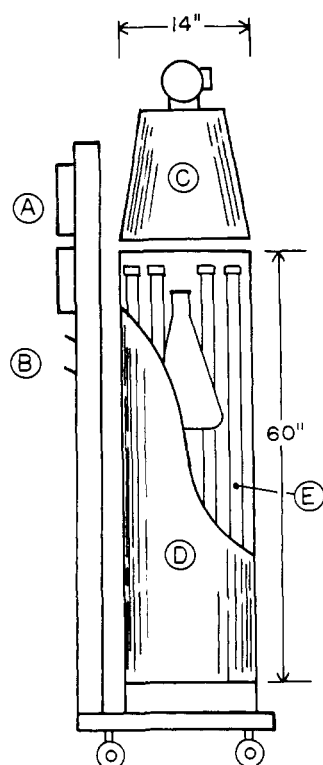


Figure 1. Large-scale photoreactor showing timers (A), control panel (B), removable hood and blower (C), irradiation chamber (D), and F40BL lamps (E).

Table I. Photodecomposition Products of 2,4,5-T

Elution temp <sup>a</sup> , °C	Identity	Conversion, % <sup>b,c</sup>
122	2,5-Dichlorophenol	<6
149	4-Chlororesorcinol	<6
154	2,4,5-Trichlorophenol	38
173	Lactone of 4,5-dichloro-2-hydroxyphenoxyacetic acid	13
198	4,6-Dichlororesorcinol	<6
	Unidentified + polymer	30

<sup>a</sup> SE-30 column. <sup>b</sup> After 200 hr in the photoreactor. <sup>c</sup> Unreacted 2,4,5-T, 92%.

A series of outdoor experiments was also conducted with 500-ml volumes of solutions (1 mg/l. and 100 mg/l.) at pH 3 and 8 and in the presence of either acetone (5 ml/l.) or riboflavin (5 mg/l.) as photosensitizers. Solutions were irradiated for about 12 hr each day for 4 days at a maximum temperature of 40°, while the similarly exposed dark-control flasks covered with aluminum foil reached 35° at midday. Acidic pH was maintained with sulfuric acid and alkaline pH was maintained with Clark-Lubs buffer (500 ml of 0.1 M boric acid in 0.1 M potassium chloride and 39.7 ml of 0.1 M sodium hydroxide/l. of deionized water).

**Chromatography.** The yellow irradiated solutions (pH 3.5) were extracted with ether and divided into neutral and acidic fractions (Moilanen and Crosby, 1972). Products were collected in glass capillary tubes after glc on an F & M Model 720 gas chromatograph equipped with a thermal conductivity detector and 2 ft × 1/8 in. (i.d.) stainless steel column containing either 6% SE-30 silicone gum or 1% diethylene glycol adipate (DEGA) on 100-120 mesh Chromosorb G. Oven temperature was programmed at

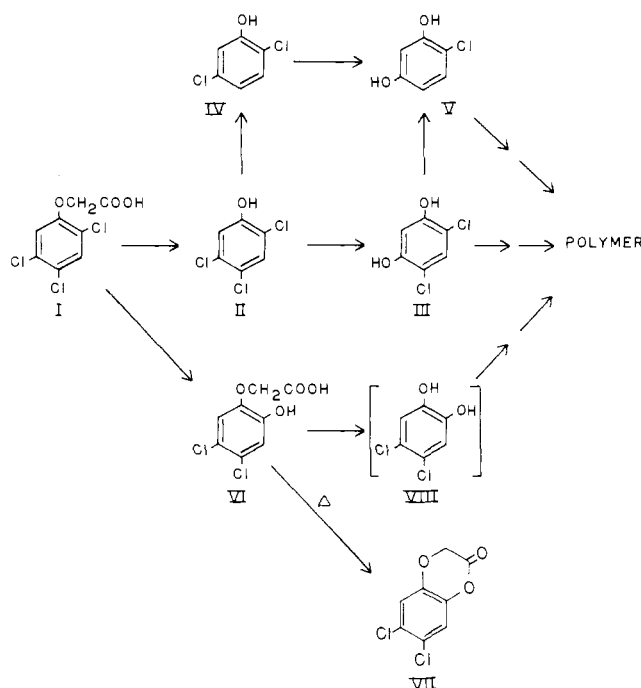


Figure 2. Proposed photodecomposition pathway for 2,4,5-T in aqueous solution.

5°/min from 75° to 200° for the DEGA column and to 250° for SE-30; helium carrier gas flow rate was 25 ml/min.

For quantitative analysis, the dried ether extracts were evaporated to dryness, methylated with ethereal diazomethane, and subjected to glc on a Varian model 1700 chromatograph, EC detector, 5 ft × 1/8 in. (i.d.) glass column, 3% SE-30 on 80-100 mesh Chromosorb W, isothermal at 180°, and N<sub>2</sub> at 20 ml/min. Values were interpolated from a satisfactory standard curve. Recoveries generally were greater than 90%.

**Identification.** The isolated products were identified by comparison of their chromatographic and spectral characteristics with those of authentic standards using a Perkin-Elmer model 337 infrared spectrometer (KBr disks) and a Varian model M-66 mass spectrometer (probe).

## RESULTS AND DISCUSSION

The products isolated from the uv irradiation of aqueous 2,4,5-T, both outdoors and indoors, are listed in Table I. All were acidic, and constituents of the neutral fraction were present in amounts too small to isolate despite the use of the efficient preparative scale photoreactor. The volatile VII was identified by its molecular ion at *m/e* 218 with the isotope cluster representing two chlorine atoms, the base peak characteristically representing loss of CO from a lactone (Barnes and Occolowitz, 1964), and infrared absorption at 1790 cm<sup>-1</sup> typical of the lactone carbonyl; the presence of this neutral compound as a constituent of the acidic fraction can be explained by dehydration of VI during glc (Cavill and Ford, 1955). Compound II represented by far the major photoproduct at any given time; attempts to detect the unstable 4,5-dichlorocatechol (VIII) were unsuccessful, although V could be isolated when the irradiated solution contained 0.5% sodium bisulfite to suppress oxidation (Crosby and Tutass, 1966).

The photodecomposition pathway shown in Figure 2 was substantiated by photolysis of II to provide III, IV, and V, although admittedly it is far from comprehensive, considering the many unidentified trace products. However, its basic features of side chain removal, replacement of ring chlorines by hydroxyl or hydrogen, and eventual formation of colored polymeric products are entirely anal-

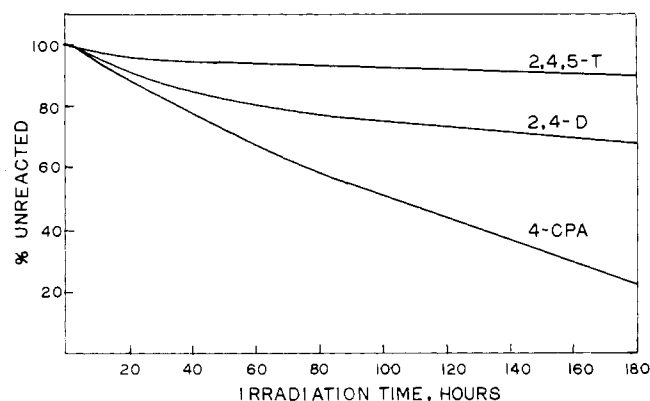


Figure 3. Relative photodecomposition rates of 4-CPA, 2,4-D, and 2,4,5-T in 100 ppm of aqueous solution. Indoor photoreactor, 30–40°, initial pH 8.

ogous to those observed in the photolysis of aqueous 2,4-D (Crosby and Tutass, 1966) and 4-CPA (Crosby and Wong, 1973). Special attention was given to the possibility of photochemical generation of the toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which might be formed from II by initial photonucleophilic displacement of the *ortho*-chlorine by trichlorophenoxide ions, followed by a second, ring-closing displacement; none was detected, possibly due to the instability of TCDD to light (Crosby *et al.*, 1971).

The rate of 2,4,5-T photolysis was somewhat more rapid at pH 8 than at pH 3 and was very slow compared to those of 4-CPA and 2,4-D (Figure 3). As expected, the unbuffered irradiated solution became increasingly acidic as photolysis progressed, and the lack of precise control over temperature and light intensity makes the curves only approximate. However, the photolysis rate of 2,4,5-trichlorophenol under the same conditions was rapid, and side chain oxidation (Crosby and Wong, 1973) was the rate-limiting step in 2,4,5-T photodecomposition.

While the isolation of verifiable photolysis products demanded the use of relatively concentrated (100-ppm) solutions, the 1-ppm levels subjected to outdoor irradiation were consistent with the higher concentrations of 2,4,5-T expected to occur in the environment (PSAC, 1971). Although the photolysis was predictably slow at both acidic and slightly alkaline pH (in buffer), the presence of low levels of acetone or riboflavin as photosensitizers (Ross and Crosby, 1973) caused a drastic increase in the rate of 2,4,5-T disappearance (Table II). Except for II, no photolysis products were identified. Although these experiments do not pretend close simulation of field conditions, agricultural drainage waters have been demonstrated to sensitize photolysis in a similar way (Ross and Crosby, 1973), perhaps even with the same sensitizers (Hunter, 1971). Sunlight actually could have a significant effect on the decomposition of 2,4,5-T in alkaline natural waters.

Table II. Photodecomposition of 2,4,5-T in Sunlight

pH		Light	Sensitizer	2,4,5-T concn		
Initial	Final			Initial, mg/l.	Final, mg/l. <sup>a</sup>	% loss
7.95	8.00			100	94	6
7.95	4.20	+		100	83	17
7.80	7.65 <sup>b</sup>			100	100	0
7.80	7.50 <sup>b</sup>	+		100	83	17
3.50	3.15			100	91	9
3.50	3.00	+		100	83	17
8.00	8.00			1.00	0.98	2
8.00	8.30	+		1.00	0.93	7
7.80	7.65 <sup>b</sup>			1.00	0.93	7
7.80	7.65 <sup>b</sup>	+		1.00	0.86	14
7.80	7.65 <sup>b</sup>		Acetone <sup>c</sup>	1.00	0.98	2
7.80	7.65 <sup>b</sup>	+	Acetone	1.00	0.20	80
7.80	7.65 <sup>b</sup>		Riboflavin <sup>d</sup>	1.00	0.84	16
7.80	7.50 <sup>b</sup>	+	Riboflavin	1.00	0.20	80

<sup>a</sup> 48 hr irradiation. <sup>b</sup> Buffered. <sup>c</sup> Acetone, 5 ml/l. <sup>d</sup> Riboflavin, 5 mg/l.

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