ratories, State College, Pa.). Column temperatures ranged from 150 to 220° (isothermal conditions) and the carrier gas flow was 40 ml/min (prepurified helium).

Photoreduction Rates. Methanol and n-butyl alcohol solutions were 10^{-4} M. Water solutions were 10^{-5} M. Samples, 10 ml each, were placed in borosilicate tubes fitted with Teflon stoppers (volume remained constant throughout the reaction period). Irradiation was carried out for periods of 1-32 hr at 300 nm at 40°. A "merry-go-round" apparatus was used to ensure equal exposure of all samples to uv irradiation. The light source used was a Rayonet reactor equipped with RUL 3000 lamps (maximum output at 300 nm) (The Southern N.E. Ultraviolet Co.).

After irradiation, 2-μl aliquots were injected in the gas chromatograph and s-triazine disappearance was measured (peak areas were measured by weight). From the amount reacted ($A_0 - A$) and the elapsed time (t) the rate constants (k) were calculated (Table II).

RESULTS AND DISCUSSION

As shown in Table II and Figures 1-4, the rate of photoreduction is dependent on at least three factors. The nature of the halogen substituent (Figures 1 and 2) has a definite influence on the rate. The value of k calculated decreases rapidly in the order I-Br-Cl-F. These results are in agreement with the known dissociation energies of the corresponding carbon–halogen bonds. The large difference between the rates for iodo- and bromo-substituted triazines and those for chloro- and fluoro-substituted ones may also be the result of the increased interaction between the nonbonding electrons on iodine and bromine with the π-system in the ring. Both these halogens are known to undergo valency shell expansion (Forbes, 1959) especially in the excited state. This heavy atom effect facilitates intersystem crossing.

The rate of reaction depends on the nature of the solvent employed as well. A decrease in k is observed when n-butyl alcohol is used instead of methanol or water. The rate of photoreaction in the latter solvents is approximately the same (Table II). This effect is probably the result of a difference in polarity of the solvents involved and of their viscosity. Polar solvents are known to decrease the energy required for π-π* transitions (Forbes, 1960).

s-Triazine	First absorption band	
	λ (methanol)	λ (1-butanol)
Simazine	268	262
Atrazine	248	244
Propazine	237	235

s-Triazines with ethyl substituents in the 4 and 6 N positions show a greater k value than those with isopropyl groups (Table II, Figures 3 and 4). The main difference in these alkyl groups is their size. As shown above, the increase in chain length results in a decreased wavelength of absorption. Steric effects are known to disturb the geometry of an excited state (Ruzo et al., 1973). This fact may explain our observations; however, further investigation is necessary in order to assess its importance in the case of s-triazine photochemistry.

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Photodecomposition of p-Chlorophenoxyacetic Acid

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Aqueous solutions of 4-CPA (p-chlorophenoxyacetic acid) decomposed readily under sunlight or laboratory ultraviolet light (300-450 nm) to provide principally p-chlorophenol, phenol, hydroquinone, p-chlorophenyl formate, phenoxyacetic acid, p-hydroxyphenoxyacetic acid, and humic acids. These products represent oxidative removal of the side chain, replacement of the chlorine by hydroxyl or by hydrogen, and polymerization of unstable intermediates. Formation of p-chlorobenzonitrile by irradiation of 4-CPA in the presence of cyanide ions substantiated that the corresponding replacement of the ring chlorine by hydroxyl was a photonucleophilic reaction.

The effects of ultraviolet (uv) light on chlorinated phenoxyacetic acids have been reported by several investigators. Kelly and Pinhey (1964) irradiated p-chlorophenoxyacetic acid (4-CPA) in ethanol with a medium-

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pressure mercury arc lamp and recovered phenol as well as o- and p-hydroxyphenylacetic acids from the migration of the side chain. Crosby and Tutass (1966) reported that irradiation of 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution with a low-pressure lamp resulted in 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,4-benzenetriol, and humic acid from processes involving mainly the removal of the side
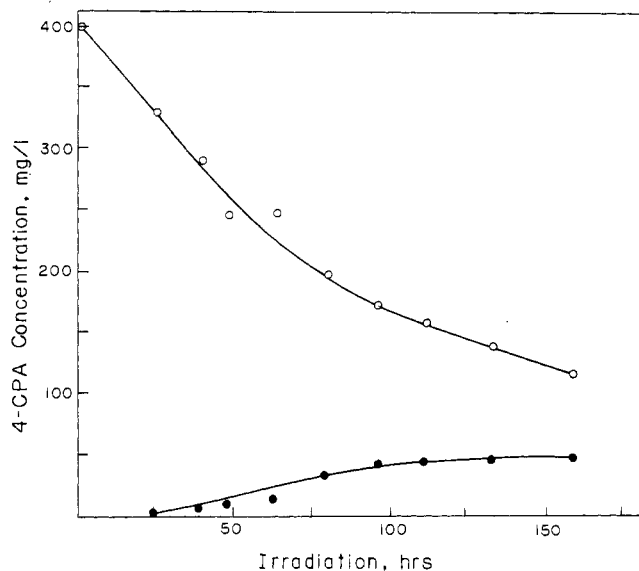
Figure 1. Photodecomposition rate of 4-CPA (O), and simultaneous formation of p-chlorophenol (●), at an initial pH of 8.0.

chain and the replacement of chlorines by hydroxyls; similar results also were obtained from irradiation of chlorophenylacetic acids (Crosby and Leitis, 1969).

Few photolysis experiments have been conducted with chlorinated phenoxyacetic acids using the low-energy uv light characteristic of natural sunlight. 4-CPA is a widely used growth regulator and the simplest of the chlorinated phenoxyacetic acids, making it an ideal model. The purpose of this investigation was to examine the effect of natural and simulated sunlight (300-450 nm) on dilute aqueous 4-CPA solutions and establish a general mechanism for the environmental photolysis of phenoxy acids.

EXPERIMENTAL SECTION

Materials. p-Bromophenol, p-chloroanisole, p-chlorobenzonitrile, p-chlorophenoxyisobutyric acid, p-chlorophenol, p-cyanophenol, hydroquinone, p-hydroxyphenoxyacetic acid, and phenol were commercial products used without further purification. 4-CPA was recrystallized three times from benzene, mp 157-158°. Humic acid was prepared previously by Crosby and Tutass (1966).

p-Chlorophenyl formate was prepared according to Van Es and Stevens (1965); mass spectrum m/e 156 (M^+), 127 (base, $M^+ - CHO$); infrared (ir) spectrum 1200, 1757 (OCHO) cm^{-1}. p-Cyanophenoxyacetic acid was obtained by the reaction of chloroacetic acid with p-cyanophenol in dilute base, mp 177-178° [Hayes and Branch (1943) reported 178.2-178.5°].

Irradiations. Standard solutions of 4-CPA (400 mg/l.), adjusted to pH 8 with aqueous sodium hydroxide, were irradiated for 65-100 hr with uv light (300-450 nm) in the presence of either air or nitrogen in a 2-l. borosilicate glass reactor (Crosby and Tang, 1969) or with natural sunlight for 7-10 days during April and May in Davis, Calif.

The brownish-yellow irradiated solutions (pH 3-4) were neutralized with dilute aqueous base and extracted three times with ether; the combined organic phases were washed with water, dried over sodium sulfate, and evaporated to a small volume on a rotary evaporator (neutral fraction). The aqueous phase was acidified to pH 2, extracted with ether, and the extract dried and evaporated as above (acidic fraction). The aqueous portion remaining after the second extraction was evaporated almost to dryness and taken up into 7:3 (v/v) methylene chloride-acetone (insoluble fraction).

The volatile photoproducts were separated and isolated by gas chromatography (glc) using a thermal conductivity

detector as described previously (Moilanen and Crosby, 1972). Most separations employed 2 ft × ¼ in. stainless steel columns packed with either 1% DEGA or 6% SE30 on 60-80 mesh Chromosorb G, helium flow rate 25 ml/min, and an oven temperature programmed from 75° to 200° at 5°/min. Acids were methylated with ethereal diazomethane before chromatography.

Other aqueous solutions were irradiated as follows: (A) p-chlorophenol (100 mg/l.), adjusted to pH 8, irradiated for 16 hr; (B) 4-CPA (400 mg/l.) in 1% sodium bisulfite, adjusted to pH 8, irradiated for 68 hr; (C) p-chlorophenoxyisobutyric acid (200 mg/l.), adjusted to pH 8, irradiated for 64 hr; (D) 4-CPA (10 g/l.) in 5% potassium cyanide containing 0.5% potassium hydroxide, irradiated for 76 hr; (E) 4-CPA (400 mg/l.) in 0.5% potassium bromide, adjusted to pH 9, irradiated for 65 hr.

Rate Measurement. Aqueous solutions containing 400 mg/l. of 4-CPA and adjusted to pH 8 or 2 were irradiated for 200 hr. The temperature was maintained at a constant 35° with a heating tape, and the voltage supply to the uv light was stabilized with a regulator. No attempt was made to control pH. Aliquots (50 ml) were withdrawn at intervals, acidified to pH 2, and extracted with ether. p-Chlorophenol was determined by glc, while unreacted 4-CPA was similarly determined after methylation. Analytical values were estimated from a standard curve for each compound. Recovery from unirradiated standards was quantitative.

Identification. Identification of all compounds except 2,4'-dihydroxybiphenyl was based on comparisons of physical properties and spectra of fractions isolated by glc with those of authentic standards. 2,4'-Dihydroxybiphenyl eluted at 200°: mp 162-163° [Omura and Matsuura (1969) reported 162-163°]; mass spectrum m/e 186 (base and M^+); ir spectrum 3600, 3400 (OH), 1600, 1525 (ϕ), 835 (p-ϕ), 770 (o-ϕ) cm^{-1}.

RESULTS AND DISCUSSION

When dilute aqueous solutions of 4-CPA (sodium salt) were irradiated in air with either uv light in the laboratory or with natural sunlight, the neutral extract yielded primarily p-chlorophenol (III) along with p-chlorophenyl formate (II) and phenol (V). The acidic extract contained only p-hydroxyphenoxyacetic acid (VII) and unreacted 4-CPA. Subsequent irradiation of p-chlorophenol yielded phenol, hydroquinone, humic acid, and a small amount of 2,4'-dihydroxybiphenyl (Experiment A). The polymeric humic acid was insoluble.

As with 2,4-D (Crosby and Tutass, 1966), inhibition of the final autoxidation step by sodium bisulfite permitted isolation of p-chlorophenol, p-chloroanisole, hydroquinone (VI), and phenoxyacetic acid (IV) (Experiment B), although control experiments showed that 4-CPA also reacted with sodium bisulfite in the dark to form p-chlorophenol and the p-chloroanisole.

The rates of photodecomposition of 4-CPA in basic solution (pH 8) and the formation of p-chlorophenol are illustrated in Figure 1. The highest observed yields of p-chlorophenol and p-chlorophenyl formate at any given time were 12 and 3%, respectively, while the other products were present in much smaller quantities. The photodecomposition rate of 4-CPA in acidic solution (pH 2) was about half that in the basic solution. Under laboratory conditions, the time for total disappearance of 4-CPA was 250-300 hr, while an equal amount of p-chlorophenol decomposed in half that time.

These observations suggest that the photodecomposition reactions of 4-CPA in water consist of three types: oxidative side chain reactions, ionic ring reactions, and condensations.

Side Chain Reactions. The rate-determining step was removal of the side chain to form p-chlorophenol, a process which depends upon the availability of oxygen and
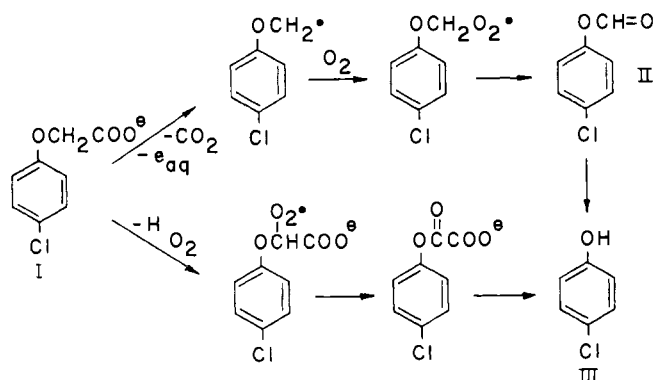
Figure 2. Mechanisms of 4-CPA photooxidation.
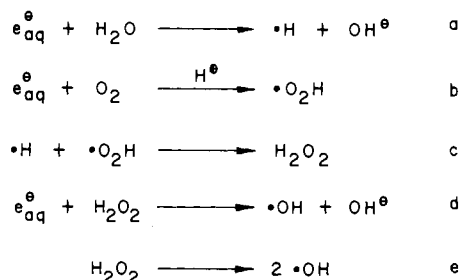

Figure 3. Radical generation from solvated electrons.

Figure 4. Proposed route of phenoxy acid photodecomposition based on 4-CPA photoproducts.

whose rate varied directly with pH. Two oxidative mechanisms are plausible (Figure 2): (a) the normal autoxidation of an ether (Walling, 1957) followed by rearrangement of the resulting peroxy radical and hydrolysis; and (b) oxygenation of the radical generated by loss of a hydrated electron and carbon dioxide from 4-CPA anion (Joschek and Grossweiner, 1966), again followed by rearrangement. The second mechanism is preferred: the predicted intermediate II was isolated, and replacement of the methylene hydrogens of the phenoxyacetic acid with methyl groups (p-chlorophenoxyisobutyric acid) still permitted the efficient formation of p-chlorophenol upon irradiation (Experiment C). However, the formation of traces of p-chlorobenzonitrile during irradiation of 4-CPA in the presence of cyanide ions (Experiment D) suggests that the p-chlorophenol observed in normal 4-CPA photolysis could be formed, in part, by nucleophilic displacement of the side chain by hydroxide ion.

The intramolecular rearrangement, proposed to involve a radical pair enclosed in a solvent cage, which produced the o- and p-hydroxyphenylacetic acids during irradiation of 4-CPA in ethanol at 254 nm (Kelly and Pinhey, 1964; Kelly et al., 1969) was not observed in our experiments (300-450 nm in aqueous solutions), perhaps due to the presence of oxygen. An ionic process also has been suggested for the rearrangement (Coppinger and Bell, 1966) but was not in evidence.

Ring Reactions. The most characteristic ring reaction was the pH-dependent replacement of the chlorine by hydroxyl or by hydrogen. These reactions were not affected by or dependent on oxygen, although similar processes have been considered by Joschek and Miller (1966) to involve free radicals. While the intensity of short wavelength uv radiation in sunlight is low, there would be sufficient quantum energy near the atmospheric cutoff (100 kcal/mol at 286 nm) to break the carbon-chlorine bond (about 80 kcal/mol) but apparently not enough for homolytic dissociation of water (116 kcal/mol). Further, the replaced chlorine appeared as Cl^- rather than Cl_2, and our specific search failed to reveal biphenyls. Hydroxylation rationalized on the basis of some energetic oxygenating species such as those generated by the hydrated electron (Figure 3) is not consistent with the lack of an oxygen dependence. The source of hydrogen to produce the dechlorinated products IV and VII has not been identified.

The reaction is better explained as a photonucleophilic substitution (Havinga and Kronenberg, 1968) in which hydroxide ion displaced chloride from the photoexcited ring, a process already known to occur under high-energy irradiation (Nijhoff and Havinga, 1965). This mechanism is supported by our observation that 4-CPA reacted readily with cyanide ions upon irradiation (Experiment D) to form p-cyanophenol and p-cyanophenoxyacetic acid analogous to the similar reaction of p-chlorophenol (Omura
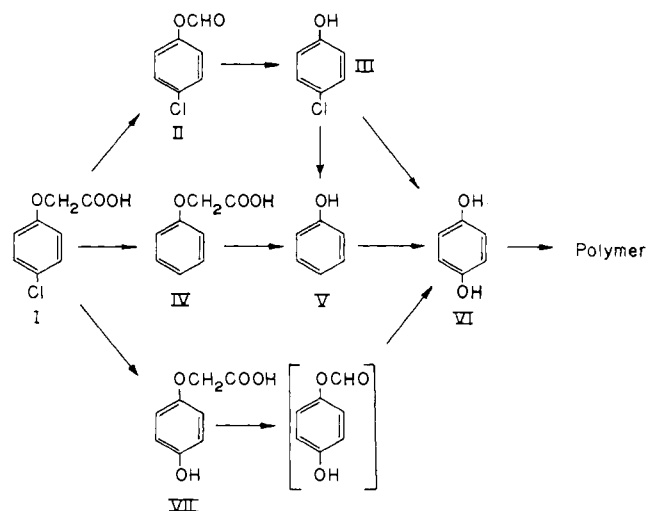
and Matsuura, 1969); a small amount of p-chlorobenzonitrile resulted from photonucleophilic displacement of the oxyacetate side chain (eq 1). In the dark, 4-CPA formed traces of p-cyanoanisole and p-chlorobenzonitrile; it reacted with potassium bromide in the light (Experiment E) to give p-bromophenol but was unreactive in the dark.

(1)
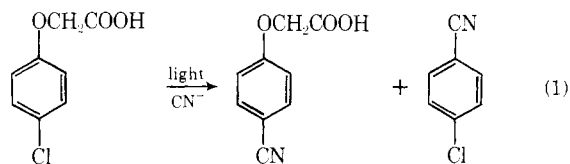
Condensations. When the irradiation of aqueous p-chlorophenol with a low-pressure mercury arc lamp was conducted at sufficiently high concentrations (>1%), hydroxylated biphenyls were produced (Omura and Matsuura, 1969). However, only traces of 2,4'-dihydroxybiphenyl were detected at the low concentrations of p-chlorophenol in our experiments (Experiment D), and none was formed from 4-CPA. The expected 4-chloro-2,4'-dihydroxybiphenyl was not observed at all.

Formation of the polymeric humic acids represented the eventual fate of 4-CPA as it did with other compounds that can be converted to quinoid products (Crosby and Leitis, 1969; Crosby and Tutass, 1966; Moilanen and Crosby, 1972). Under field conditions, this polymerization probably would involve both ionic and oxidative combination with other substances in contact with the quinoid intermediates to form a variety of polymer types representing, in part, the carbon atoms of the original 4-CPA ring.

The products identified and the mechanisms proposed for their formation suggest the photolysis pathway for

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

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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 (Bamesberger 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 μW/cm^2 at the center of the chamber and 785 μW/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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