Photodecomposition of Chlorobenzoic Acids

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Ultraviolet irradiation of 2-, 3-, and 4-chlorobenzoic acids as aqueous solutions of their sodium salts led to replacement of the chlorine by hydroxyl and hydrogen to produce the corresponding hydroxybenzoic acids and benzoic acid itself. In the case of the 4-chloro isomer, conversions to benzoic acid reached 90%. A mixture of 4-acetylbenzoic acid and terephthalic acids also was formed. In sunlight, the monochlorobenzoic acids remained unaffected, while amiben (3-amino-2,5-dichlorobenzoic acid) decomposed rapidly.

Previous work (Crosby and Tutass, 1966) has demonstrated that the widely used herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) undergoes photodecomposition in aqueous solution. The key reaction in the eventual complete transformation of 2,4-D to polymeric humic acid was the photochemical replacement of the chlorine atoms of the aromatic ring by hydroxyl groups.

Although amiben (3-amino-2,5-dichlorobenzoic acid) is easily photolyzed in aqueous solution (Sheets, 1963), the chlorinated benzoic acids as a general class of herbicides similar to the phenoxy acids in many chemical and biological properties might be expected to have greater environmental stability due to deactivation of the ring by the carboxyl group. The present investigation was conducted to determine the stability of the otherwise unreactive ring chlorines of model chlorobenzoic acids under photolyzing conditions in aqueous solution in the laboratory and in sunlight.

EXPERIMENTAL

Materials. The halogenated benzoic acids and other standard organic compounds were reagent grade commercial products homogeneous on thin-layer chromatography. Organic solvents were redistilled shortly before use. Acids were esterified for gas chromatographic determination and comparison by reaction with an ethereal solution of diazomethane. Amiben (3-amino-2,5-dichlorobenzoic acid) was an analytical standard (Amchem Products, Inc., Ambler, Pa.).

4-Acetylbenzoic acid was prepared by reaction of a suspension of p-diacetylbenzene (Aldrich Chemical Company) in 10% aqueous sodium hydroxide solution with an excess of a reagent prepared by dissolving 9.0 grams of iodine and 18.3 grams of potassium iodide in 75 ml. of water. After 10 minutes, the homogeneous solution was made strongly alkaline with sodium hydroxide, filtered, the filtrate was extracted with chloroform, and the upper aqueous phase was decanted and acidified. A precipitate of highly-insoluble terephthalic acid was removed by filtration, this filtrate was extracted with several portions of ether, the decanted ether layer was evaporated to dryness, and the brown residue was triturated with chloroform to remove most of the color. The tan residue (m.p. 196° C.) was sublimed (ca. 200 Torr.) to provide a small yield of 4-acetylbenzoic acid, m.p. 207° to 209° C. (lit. 208°, Heilbron, 1965).

Irradiation. Solutions for irradiation were prepared by dissolving the desired acid in demineralized water, containing a small excess of sodium hydroxide, to provide a concentration of 100 mg. per liter. The pH of the solution was adjusted with a small amount of dilute sulfuric acid or aqueous sodium hydroxide if desired. Results were checked with solutions prepared from recrystallized sodium chlorobenzoates.

The solutions were irradiated in open dishes in outdoor sunlight or under a 360-watt mercury arc lamp as previously described (Crosby and Tutass, 1966). The temperature was maintained at $25 \pm 2°$ C. by circulation of ice-cold water through immersed glass cooling coils or by an external cold bath. Alternatively, solutions were irradiated with a low-pressure mercury arc lamp in the reactor described by Henderson and Crosby (1967), the temperature being maintained at 25° C. by circulating water through the cooling jacket of the apparatus. In all cases, the solutions were continuously stirred magnetically. The duration of most indoor irradiations was three hours, while experiments in sunlight required up to 14 days. Unirradiated controls were examined in every instance.

Extraction and Separation. The irradiated solutions were extracted with ether, and the extracts were separated into acidic and neutral fractions as described previously. Ether extractables were subjected to thin-layer chromatography (TLC) on silica gel G plates developed with solvent A in the case of 2-chloro- and 3-chlorobenzoic acids and with solvent C in the case of 4-chloro- and 3-bromobenzoic acids. Strips of the developed plates were sprayed with diazonium reagent, and the detected phenolic bands were scraped off, eluted with acetone, and the eluates evaporated to dryness at ambient temperature. Ultraviolet-absorbing compounds also were detected on chromatoplates by their quenching of the fluorescence of the phosphor incorporated in the adsorbent.

Methylated acidic fractions and the neutral fractions were subjected to gas-liquid chromatography (GLC) on a 2-ft. by $1/_8$-in. column containing 20% Dow 11 silicone oil on 70- to 80-mesh Chromosorb W. Generally, an F and M Model 720 gas chromatograph with thermal conductivity detector was

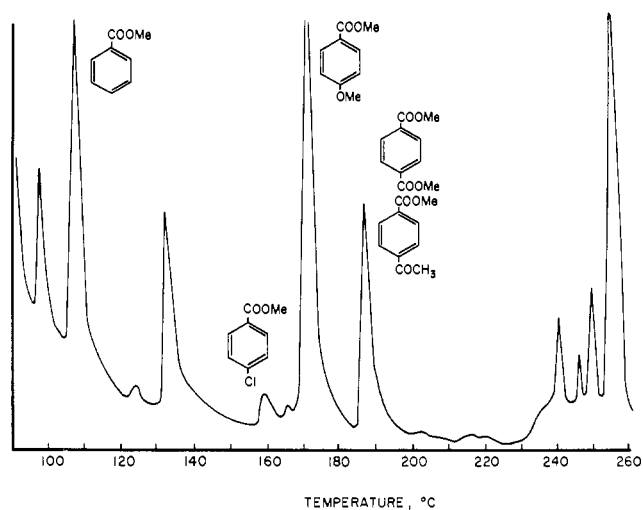Department of Environmental Toxicology, University of California, Davis, Calif. 95616

Figure 1. Gas chromatogram of methylated acidic ether extract from sodium 4-chlorobenzoate irradiated in aqueous solution

employed, and programmed-temperature measurements were made at an increase of 7.5° C. per minute. Some fractions also were checked for chlorinated constituents on a Dohrman Model G-100 gas chromatograph equipped with a micro-coulometric detector and a 6-ft. by ¼-in. glass column containing 10% SE-30 gum rubber on 60- to 80-mesh Chromosorb W.

Individual constituents resolved by GLC were isolated by inserting the small end of a Pasteur pipet through a Neoprene septum into the exit port of the chromatograph as the desired fraction emerged. Collections were improved by heating the lower portion of the pipet on a warm hot-plate while chilling the top portion with solid carbon dioxide. Detector filaments generally were turned off during collections to avoid possible thermal decompositions. Collected fractions were purified by rechromatography, and their infrared spectra were measured in KBr disks with a Perkin-Elmer Model 337 Infrared Spectrophotometer and compared with those of known compounds also collected from the gas chromatograph under identical conditions.

Mass spectra were measured with an AEI Model MS-9 high resolution mass spectrometer equipped with a heated inlet.

Thin-layer chromatography was conducted on silica gel G containing zinc silicate phosphor. Solvents were mixed according to volume: solvent A was toluene–dioxane–acetic acid (6:2:1); solvent B was hexane–acetone (4:1); solvent C was 1-butanol saturated at 25° C. with water; solvent D was benzene–acetic acid–water (2:2:1, upper phase); and solvent E was ethanol–ammonium hydroxide–water (20:1:4). Adsorbed compounds were detected by quenching of the fluorescence of the phosphor, by spraying with 1% aqueous potassium permanganate solution, or by spraying with a 1% solution of 4-nitrobenzenediazonium fluoborate in 20% aqueous sodium acetate.

RESULTS

None of the three isomeric chlorobenzoic acids gave rise to neutral or alkaline products upon irradiation with sunlight or ultraviolet light, although extracts were checked by TLC and by GLC with both thermal conductivity and microcoulo-metric detectors. TLC of the acidic extract in solvent A followed by treatment with diazonium reagent revealed a single yellow-brown band corresponding in R_f to the expected hydroxybenzoic acid in each instance. 3-Bromobenzoic acid gave results identical to those from its chloro analog.

Table I. Mass Spectrum of the 192° Fraction

Ion	Formula	Mass Calcd	Mass Found
(benzene ring with COOCH₃ top and COOCH₃ bottom, +)	$C_{10}H_{10}O_4$	194.0579	194.0598
(benzene ring with COOCH₃ top and COCH₃ bottom, +)	$C_{10}H_{10}O_3$	178.0630	178.0630
(benzene ring with COOCH₃ top and CO⊕ bottom)	$C_9H_7O_3$	163.0395	163.0390
(benzene ring with CO⊕ top and COCH₃ bottom)	$C_9H_7O_2$	147.0446	147.0456
(benzene ring with COOCH₃ top, ⊕ bottom)	$C_8H_7O_2$	135.0446	135.0449

The methylated acidic fraction of photolyzed 4-chloro-benzoic acid was examined in detail by GLC. In addition to minor constituents, major fractions were eluted at 138°, 160°, 177°, and 192° C. (Figure 1). Other fractions were not explored. Comparison of elution temperatures and infrared spectra of each purified constituent showed the 138° C fraction to be methyl benzoate resulting from reductive dechlorination of the starting material to benzoic acid. The smaller 160° C. fraction represented the methyl ester of unreacted 4-chloro-benzoic acid, revealing that almost all of the starting material had been converted to other products during the 3-hour irradiation. The major fraction, eluted at 177° C., was identical with methyl 4-methoxybenzoate representing the 4-hydroxybenzoic acid formed by replacement of the ring chlorine by hydroxyl.

The fraction which was eluted at 192° C. was obtained as a white crystalline solid after repeated GLC purification. It melted over a narrow range, and the IR spectrum showed absorption frequencies representing two different types of carbonyl group (1730, 1680 cm.⁻¹), the first of which was characteristic of the expected methyl ester group. The high-resolution mass spectrum indicated a mixture of two compounds having respective masses of 178 and 194. Determination of the exact masses of several major fragments (Table I) revealed that the 192°C. fraction was a roughly 1:3 mixture of methyl 4-acetylbenzoate and dimethyl terephthalate. Methylation of various mixtures of the two acids followed by GLC provided only the single fraction which was eluted at 192° C.

This fraction was collected from GLC and subjected to TLC in solvent B. Ultraviolet-absorbing bands appeared at R_f 0.22 and 0.32, corresponding exactly with those produced by authentic methyl 4-acetylbenzoate and dimethyl terephthalate, respectively. Under the same conditions, methyl 4-chloro-benzoate appeared at R_f 0.75 and methyl 4-methoxybenzoate at R_f 0.64. The band at R_f 0.32, eluted from the TLC plate, provided an infrared spectrum and GLC elution temperature identical with those of dimethyl terephthalate; the R_f 0.22 band likewise was identical with authentic methyl 4-acetyl-benzoate.

To assure that these acids were not artifacts, the acidic extracts from each of several irradiation experiments with 4-chlorobenzoic acid were subjected to TLC in solvent C. The resulting bands, detected by fluorescence quenching, corresponded to terephthalic acid (R_f 0.04), 4-acetylbenzoic acid (0.26), 4-chlorobenozic acid (0.44), 4-hydroxybenzoic acid (0.49), and several minor unidentified compounds (0.09, 0.15). Identity was verified by rechromatography and comparison with standards in two additional solvents, D and E.

For comparison, an aqueous solution of amiben (sodium salt) rapidly became yellow-brown upon exposure to sunlight. GLC analysis of the methylated acidic extract produced only a single volatile product, which proved to be identical with amiben in its spectral and chromatographic characteristics. However, TLC of the photolysis mixture resulted in at least 12 colored bands upon treatment with the diazonium reagent (Crosby, 1966). Irradiation with the mercury arc caused destruction of amiben within a few minutes and no photodecomposition products could be resolved.

DISCUSSION

Among the economically important benzoic acid herbicides are TBA (principally 2,3,6-trichlorobenozic acids with smaller amounts of other chlorobenzoic acids), PBA ("polychlorobenzoic acids" containing 2 to 5 chlorines), amiben (3-amino-2,5-dichlorobenzoic acid) and dicamba (3,6-dichloro-2-methoxybenzoic acid); DCPA and Glenbar are esters of 2,3,5,6-tetrachloroterephthalic acid. The complexity of the potential photodecomposition products to be expected from these compounds suggested the prior investigation of simple models.

As observed previously with the chlorinated phenoxyacetic acids, irradiation of chlorobenzoic acid salts with ultraviolet light at 254 mμ brought about the replacement of the ring halogen by hydroxyl. The reaction was rapid in either the o-, m-, or p- position, and bromobenzoic acids responded in an identical manner. The absence of halobenzenes in the neutral fraction indicated that decarboxylation does not occur during photolysis of the monochlorobenzoic acids.

The photochemical reductive dehalogenation of chlorinated aromatic compounds in aqueous solution appears not to have been described prior to our initial report (Crosby, 1966), although the formation of chloride ions during irradiation of chlorobenzoic acids in alcohols (Szychlinski, 1960; Walczak and Szychlinski, 1963) could be due to this reaction. The requirement for light normally suggests the operation of a free-radical mechanism in which hydrogen atoms are transferred from solvent water; failure to detect chlorobenzene, 4,4'-dichlorobiphenyl, biphenyl-4,4'-dicarboxylic acid, or other products expected from a free-radical reaction may be due to the very large molar proportion of water compared to solute or, perhaps, to an ionic mechanism. Nonetheless, at alkaline pH the reduction product (benzoic acid) represented at least 90% of the total photolyzate mixture in the case of 4-chlorobenzoic acid and appeared to be stable to further photolysis under these experimental conditions (compare Joschek and Grossweiner, 1966).

Although always present in amounts far less than the hydroxylated and hydrogenated products, the presence of 4-acetylbenzoic acid and terephthalic acids in the reaction mixture is significant. In addition to the difficulties of identification raised by the consistent occurrence of these compounds or their methyl esters as a single, homogeneous substance, their formation demonstrates the possibility that completely unexpected products may result from photolysis. Although it is possible that terephthalic acid is derived from reaction of the aromatic halogen compound with carbonate ion in the surrounding medium, the source of the acetyl group in 4-acetylbenzoic acid is obscure even after extensive investigation.

Benzoates and their simple chlorinated and hydroxylated derivatives absorb ultraviolet light at wavelengths well below 290 mμ (Doub and Vandenbelt, 1947, 1949). While sufficient energy to break C—Cl bonds can be derived from sunlight, it is not surprising that the longer wavelengths reaching the earth's surface do not appear to affect sodium chlorobenzoate solutions. The herbicidal polychlorobenzoic acids such as TBA may be expected to be resistant to photolysis in aqueous solution in the environment; indeed, they remain impassive to light even in the presence of sensitizers such as riboflavin (Hamilton and Aldrich, 1953), and the persistence of this class in the greenhouse and field is notably greater than that of corresponding phenoxacetic acids (Minarik *et al.*, 1951; Sheets *et al.*, 1968).

A few herbicidal benzoic acid derivatives absorb ultraviolet light in the region about 290 mμ, however. Amiben, for instance, exhibits a wavelength maximum of 297 mμ in aqueous solution (Bailey and White, 1965); sunlight causes this herbicide to decompose readily in aqueous medium with the formation of reduced (and, probably, hydroxylated) products (Plimmer, 1967). Chlorobenzoic acids also are rapidly photoreduced in methanol solution, and amiben, TBA, and the related dichlobenil (2,6-dichlorobenzonitrile) were preferentially reduced in the 2-position (Plimmer and Hummer, 1968, 1969). Indeed, where multiple chlorines are present, replacement of either or both halogens by hydroxyl or hydrogen is to be expected, and the eventual formation of polyhedric phenols in this way finally leads to polymer formation, as was the case with 2,4-D.

LITERATURE CITED

Bailey, G. W., White, J. L., *Residue Reviews* (F. A. Gunther, ed), 10, 97–122 (1965).
Crosby, D. G., Tutass, H. O., J. AGR. FOOD CHEM. 14, 596–99 (1966).
Doub, L., Vandenbelt, J. M., *J. Amer. Chem. Soc.*, 69, 2714–23 (1947).
Doub, L., Vandenbelt, J. M., *J. Amer. Chem. Soc.*, 71, 2414–20 (1949).
Hamilton, R. H., Aldrich, R. J., *Weeds*, 2, 202–3 (1953).
Heilbron, I., Ed., "Dictionary of Organic Compounds," Vol. 1, p. 13, Oxford, New York, 1965.
Henderson, G. L., Crosby, D. G., J. AGR. FOOD CHEM. 15, 888–93 (1967).
Joschek, H.-I., Grossweiner, L. I., *J. Amer. Chem. Soc.*, 88, 3261–8 (1966).
Minarik, C. E., Ready, D., Norman, A. G., Thompson, H. E., Owings, J. F., Jr., *Botan. Gaz.* 113, 135–47 (1951).
Plimmer, J. R., U.S. Department of Agriculture, Beltsville, Md., personal communication, October 1967.
Plimmer, J. R., Hummer, B. E., *Abstr. 8th Meeting, Weed Sci. Soc. Amer.*, p. 20, New Orleans, La., 1968.
Plimmer, J. R., Hummer, B. E., J. AGR. FOOD CHEM. 17, 83 (1969).
Sheets, T. J., *Weeds*, 11, 186–90 (1963).
Sheets, T. J., Smith, J. W., Kaufman, D. D., *Weed Sci.*, 16, 217 (1968).
Szychlinski, J., *Rocz. Chem.*, 34, 941–6 (1960).
Walczak, M., Szychlinski, J., *Zeszyty Nauk. Mat., Fiz., Chem., Wyzsza Szkola Pedagog. Gdansk*, 3, 117–21 (1963).