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Photolysis of Isopropyl 3-Chlorocarbanilate in Water

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Photolysis of isopropyl 3-chlorocarbanilate (CIPC) in distilled water at 25 °C using simulated noonday sunlight afforded isopropyl 3-hydroxycarbanilate (3-HOIPC) as the only major photolysis product. Half-life for the disappearance of CIPC under these conditions was 130 h. A second major photolysis product, 2-isopropoxycarbonylamino-1,4-benzoquinone, was obtained when the photolysis was performed in 2% aqueous acetone.

Isopropyl 3-chlorocarbanilate (CIPC) is a widely used herbicide for the control of annual grasses and broadleaved weeds in alfalfa, soybeans, clover, and garden vegetable crops. As part of a program to determine the fate of CIPC in the environment, a study of its photolysis in water was undertaken.

EXPERIMENTAL SECTION

Materials. CIPC was PPG Industries' technical material recrystallized from heptane, mp 38–40 °C. ^{14}C ring-labeled CIPC was obtained from New England Nuclear, 4.3 mC/mmol. Water was distilled from potassium permanganate. Isopropyl 3-hydroxycarbanilate was prepared from 3-aminophenol and isopropyl chloroformate (Schering, 1966), mp 80–82 °C. All solvents were analytical or reagent grade.

Apparatus. The photochemical cell had a capacity of 1050 mL. It was equipped with a standard water-cooled photochemical quartz immersion well and magnetic stirring bar. Light source was a Hanovia 654A high-pressure mercury vapor lamp filtered with a Hanovia 7740 Pyrex sleeve. The assembled unit was contained in a constant temperature water bath. The reactor was open to the atmosphere during photolysis.

Analysis. High-pressure liquid chromatography (HPLC) was performed with a du Pont Model 830 liquid chromatograph using a Zorbax ODS column (mobile phase, 60% methanol in water; column temperature, 55 °C; pressure, 1500 psig; flow rate, 0.2 mL/min). Liquid scintillation counting (LSC) utilized a Packard Model 3003 Tri-carb liquid scintillation spectrophotometer. Thin-layer chromatography (TLC) was carried out using 20 × 20 cm silica gel 60 F-254 plates of 0.25 mm thickness with fluorescent indicator (EM Laboratories). The plates were developed two-dimensionally using 60:40 hexane–acetone and 90:9:1 chloroform–acetone–acetic acid (v/v). Autoradiographs were obtained by exposing the TLC plates to Kodak SB54 single-coated, blue-sensitive, medical x-ray film. NMR spectra were run on Varian DA60IL or Varian CFT20 spectrometers. Infrared spectra were determined on Perkin-Elmer 521 or Perkin-Elmer Infracord spectrophotometers. Mass spectra were recorded on a Finnigan 1015D spectrometer.

Procedure. Two microcuries of ^{14}C ring-labeled CIPC dissolved in 40 μL of benzene was purified by TLC. The TLC scrapings containing purified [^{14}C]CIPC were placed in 1100 mL of water together with sufficient nonradioactive CIPC to obtain a 4 ppm solution. The solution was stirred for 64 h and filtered. The bulk of solution (1050 mL) was placed into the photochemical reactor, and the remaining 50 mL was set aside as a dark control. The photolysis solution was photoirradiated at 25 °C for 104 h. During this period, samples were periodically withdrawn and analyzed by HPLC, LSC, and extraction with methylene chloride (CH_2Cl_2), followed by TLC/autoradiography (AR) of the CH_2Cl_2 extracts. Half-life for the disappearance of CIPC was calculated from LSC data of appropriate HPLC fractions.

A solution containing 124 ppm CIPC was prepared by saturating 1 L of 2% aqueous acetone with nonradioactive CIPC for the photolysis of CIPC in aqueous acetone. This solution was filtered and then photoirradiated for 7 h. Samples of the solution were periodically withdrawn during the photolysis, extracted with CH_2Cl_2, and analyzed by TLC. After 3 h ca. 50% of the CIPC had disappeared and two major extractable photolysis products were observed.

Product Isolation and Identification. Isopropyl 3-hydroxycarbanilate (3-HOIPC) was isolated by CH_2Cl_2 extraction of several 50 ppm nonradioactive CIPC photolysis solutions followed by prep-scale TLC. Infrared, NMR, and mass spectra were identical with those of authentic 3-HOIPC.

2-Isopropoxycarbonylamino-1,4-benzoquinone (IBQ) was isolated from a photolysis solution of 2000 ppm CIPC in 20% aqueous acetone. Recovery involved extraction with CH_2Cl_2, elution chromatography, and prep-scale TLC. Ten milligrams of bright-yellow crystalline IBQ, mp 66–68 °C, was obtained in this manner: IR (mull), 1720 (carbamate C=O), 3290 (NH), 1665 (quinone C=O), 1635 cm^{-1} (C=C conjugated with C=O); NMR (Fourier transform, CCl_4/$CDCl_3$) δ 1.3 (d, 6, isopropyl methyls), 5.0 (sept, 1, isopropyl

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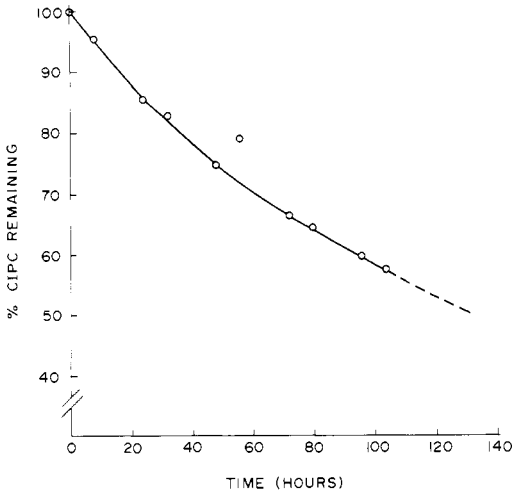

Figure 1. Decline curve for isopropyl 3-chlorocarbanilate during photolysis in water at 25 °C.

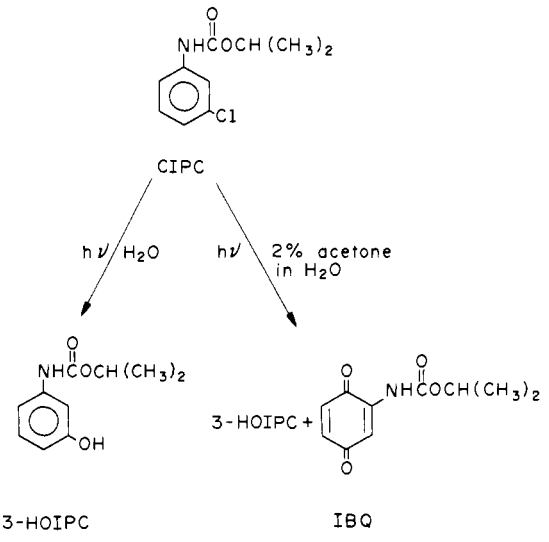

Figure 2. Products of isopropyl 3-chlorocarbanilate photolysis.

methine), 6.7 (s, 2, ring H-5 and H-6), 7.2 (s, 1, ring H-3), 7.4 (br s, 1, NH); MS *m/e* (rel intensity) 209 (5, M^+), 167 (16), 150 (9), 123 (12), 95 (13), 43 (100), and 41 (28). Fragments 167, 150, 123, 43, and 41 are typical of isopropyl carbamates and correspond to $C_6H_3O_2NHCO_2H$, $C_6H_3O_2NCOH^+$, $C_6H_3O_2NH_2$, $(CH_3)_2CH^+$, and $CH_2{=}CHCH_2^+$, respectively. Fragment 95 represents loss of ring CO from $C_6H_3O_2NH_2$, which is a very typical fragmentation pathway for *p*-benzoquinones.

RESULTS AND DISCUSSION

In an attempt to approximate field conditions, photolysis of CIPC was examined in the presence of simulated noonday sunlight. These conditions were achieved in the laboratory with a mercury vapor lamp fitted with a Pyrex sleeve. This unit provided light between 280–1400 nm.

CIPC was expected to be stable to simulated sunlight, since it has negligible absorption above 280 nm. However, at a concentration of 4 ppm in water at 25 °C the half-life for disappearance of CIPC was 130 h of simulated noonday sunlight (Figure 1).

Initially, only CIPC was observed in the photolysis solution by HPLC and TLC/AR. However, as the photolysis progressed, a second extractable radioactive material was observed by AR. This material was shown to be a photolysis product by virtue of its absence in the dark control. It was initially identified as 3-HOIPC by instrumental analysis of a sample isolated from a 50 ppm cold CIPC photolysis solution. Evidence confirming its presence in the radioactive photolysis solution was then obtained by TLC/AR and HPLC using authenic 3-HOIPC as a standard.

Photostability of 3-HOIPC under these conditions was greater than that of CIPC, since it increased in concentration as the photolysis progressed. This observation was further substantiated by direct photolysis of authentic 3-HOIPC in water.

Replacement of a ring chlorine by a hydroxyl moiety in water in the presence of light has been previously reported. Moilanen and Crosby (1972) reported the photolysis of propanil (3,4-dichloropropionanilide) in water gave hydroxychloro- and dihydroxyanilides, whereas Crosby and Tutass (1966) reported the photolysis of 2,4-D (2,4-dichlorophenoxyacetic acid) in water led to the formation of hydroxychlorophenoxyacetic acids.

The photolysis was carried out to 42% conversion of CIPC. At no time were any other extractable photolysis products detected other than 3-HOIPC. However, the amount of ^{14}C activity remaining in the aqueous fraction, after extraction of the photolysis solution, increased from nil at time zero to 10% after 104 h of photoirradiation. Attempts to characterize this activity by continuous extraction of the aqueous fraction followed by TLC/AR revealed the presence of only 3-HOIPC and a trace of CIPC. Furthermore, direct analysis of the aqueous fraction by TLC/AR disclosed the presence of polymeric material based on its lack of mobility on the TLC plate. LSC of TLC plate scrapings of this immobile material showed 65% of the ^{14}C activity in the aqueous fraction (6.5% of initial ^{14}C activity) was due to polymeric material. The amounts of unextracted 3-HOIPC and CIPC in the aqueous fraction were also determined in this manner and found to be 12 and 0.4% (or 1.2 and 0.04% of the initial ^{14}C activity), respectively. Further evidence supporting the presence of polymeric material was obtained by column chromatography using Sephadex G-50 resin. This indicated the polymeric material ranged from 3000 to 30000 in molecular weight. Polymeric photoproducts have also been reported for the photolysis of ethylcarbanilate in organic solvents (Masilamani and Hutchins, 1976; Bellus and Schaffner, 1968) and propanil in water (Moilanen and Crosby, 1972).

Although anilines have been reported as photolysis products of *N*-phenylcarbamates in organic solvents (Masilamani and Hutchins, 1976), no chloroaniline was observed during the photolysis of CIPC in water. This was based on inability to detect chloroaniline by extraction/TLC/AR of the photolysis solution after it was made slightly basic (pH 7.2).

Formation of volatile ^{14}C ring-labeled photolysis products was negligible, since total ^{14}C activity in the photolysis solution remained relatively constant throughout the photoirradiation period.

Water obtained from natural sources contains dissolved substances which may act as sensitizers for photochemical reactions. Therefore, the photolysis of CIPC was also examined in aqueous acetone, since differences in products and reaction rates may be observed between sensitized and unsensitized photochemical reactions.

Acetone has been suggested as a triplet sensitizer that can mimic the sensitizing effect of dissolved materials present in natural waters (Train, 1975). Ross and Crosby (1973) reported ethylenethiourea photodegraded rapidly in water in the presence of acetone in sunlight, but no photolysis occurred in the absence of acetone. Plimmer (1972) reported the photolysis of heptachlor in acetone produced a cage product, whereas in hexane, two isomeric

products were formed by dechlorination of the double bond, but no cage compound was obtained. In the case of CIPC, addition of 2% acetone to the photolysis solution not only increased the rate of CIPC disappearance ca. 30-fold, but also gave rise to a second extractable photolysis product, identified as IBQ, in addition to 3-HOIPC.

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A New Degradation Product of the Insecticide Mexacarbate Found in Fresh Water

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The carbamate insecticide mexacarbate (4-dimethylamino-3,5-xylyl methylcarbamate) is degraded in plants and animals by oxidation of the dimethylamino group and by hydrolysis of the carbamate moiety. In water solutions of different pH values, essentially the same degradation products were found: 4-methylamino-3,5-xylyl methylcarbamate, 4-amino-3,5-xylyl methylcarbamate, 4-methylformamido-3,5-xylyl methylcarbamate, 4-formamido-3,5-xylyl methylcarbamate, and 4-dimethylamino-3,5-xylyl hydroxymethylcarbamate. Additional products identified included 4-dimethylaminoxylenol and 2-hydroxy-3,5-dimethyl-*p*-benzoquinone, a new degradation product. Bioassay of this new degradation product on sixth stage western spruce budworm (*Choristoneura occidentalis* Freeman) larvae indicated little or no toxicity at the rate of 0.1 mg/g body weight by topical application and 0.05 mg/g body weight by injection.

Mexacarbate has been used widely to control the western spruce budworm (*Choristoneura occidentalis* Freeman) in forest environments. Therefore, it is important that as many of the degradation products as possible found in water be identified so their toxicity to insects and other animals can be determined.

This paper reports the isolation and identification of some products formed from mexacarbate exposed to aquatic conditions and the toxic effects of a hydrolytic product on the western spruce budworm.

Schmiege et al. (1970) reported on the toxic effects of some of the oxidation products of mexacarbate of this highly destructive forest pest. Other studies have shown that mexacarbate is degraded by various substrates to several oxidative products. All of these products have the ring and carbamate moiety intact (Abdel-Wahab et al., 1966; Oonnithan and Casida, 1966; Abdel-Wahab and Casida, 1967; Tsukamoto and Casida, 1967; Roberts et al., 1969).

During a study of the effects of forest soil and water microorganisms on mexacarbate, Dickerson (1975) found that a pink color developed in the control flasks containing only water and mexacarbate. This observation was made several times. Colored products in the form of azo compounds have been identified by others working with anilide herbicides (Bartha and Pramer, 1967; Bartha et al., 1968; Bartha, 1968, 1969; Briggs and Ogilive, 1971). Our literature search did not reveal similar information dealing with carbamate insecticides. However, several workers have reported on the degradation of mexacarbate in aqueous environments (Knaak, 1971; Eichelberger and Lichtenberg, 1971) and the effects of mexacarbate on microbial activity in forest soil (Bollen et al., 1970) and in water and soil (Benezet and Matsumura, 1974; Dickerson, 1975).

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METHODS AND MATERIALS

Production of Degradation Products. We prepared 100 mL of 0.2% (w/v) 99.6% pure mexacarbate in tap and distilled water in solutions with differing pH values—4.5, 6.5, 7.5, and 9.5.

The buffer solution contained 2.2 mM potassium phosphate, 7.6 mM ammonium sulfate, 0.4 mM magnesium sulfate, and 1.9 mM potassium nitrate. These solutions were left exposed to air and laboratory fluorescent lighting or sunlight. At various time intervals, 10-mL aliquots were removed and a preliminary analysis was made by thin-layer chromatography (TLC) for degradation products. The water used in these studies was not sterilized because Dickerson (1975) compared the effects of sterilized and nonsterilized water and found that degradation occurred in both conditions. Development of the colored product was monitored by reading absorption at 513 mμ in a B & L Spectronic 20 spectrophotometer.

In an attempt to understand the mechanism involved in the various pathways of degradation of mexacarbate,

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