Figure 3. Autoradiogram of ETU photolysis on silica gel.

(Table II). Of these, only 2-imidazolidone and bis(imidazolin-2-yl) sulfide have been identified by comparison of R_f values in four different solvent systems (Table III). Table II also gives the amount of the various components following 20 hr of exposure to the GE sunlamp.

2-Imidazolidone has been reported to undergo photooxidation to hydantoin (Ingamells, 1963). However, hydantoin has not been detected among the ETU photodecomposition products, nor did irradiation of 2-imidazolidone on silica gel afford any of the other products of ETU photolysis.

The ninhydrin positive components of ETU photolysis remain unidentified. Although component no. 3 (Figure 3) has an R_f value identical to glycine, attempts to detect a dinitrophenyl derivative (Levy and Chung, 1955) or the volatile N-trifluoroacetylglycine methyl ester (Cruickshank and Sheehan, 1964) were unsuccessful.

ETU is much more stable toward photolysis in aqueous solution. Irradiation at an intensity of 1900 $\mu W/cm^2$ for 24 hr gave an insignificant loss (<5%); however, irradiation at 3300 $\mu W/cm^2$ for 15 days resulted in a 33% loss of

Table IV. Sensitized Photodecomposition of ETU in Aqueous Solution; 24-hr Exposure at 1900 $\mu W/cm^2$

Photosensitizer	% loss	Photosensitizer	% loss
	< 5	Flavone	10
1-Acetonaphthone	30	Eosin	10
1-Naphthaldehyde	30	Benzophenone	10
Methylene blue	30	Acetophenone	<10
2-Acetonaphthone	20	Crystal violet	<10

ETU. Addition of photosensitizers to the aqueous solution again enhanced the rate of photolysis; results are summarized in Table IV. The aqueous solution experiments were discontinued upon publication of work by Ross and Crosby (1972).

From the results of this work, it is apparent that photochemical degradation can play an important role in the removal of ETU from the environment. Still to be determined, however, is the nature and fate of the ninhydrin positive components (Zone B, Figure 3) which constitute a major portion of the photolysis products on silica gel.

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Photolysis of Ethylenethiourea

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Ethylenethiourea (ETU) in aqueous solution (0.5-50 ppm) was stable to sunlight. However, in the presence of dissolved oxygen and sensitizers such as acetone or riboflavin, it was rapidly photooxidized via ethyleneurea and glycine sulfate.

ETU decomposition also occurred in boiled samples of agricultural drainage waters in sunlight but not in the dark, indicating that natural photosensitizers may play an important part in the environmental transformations of xenobiotics.

Ethylenethiourea (2-imidazolidinethione, ETU) occurs as an impurity in technical ethylene bisdithiocarbamate fungicides as well as from both their metabolic (Engst and Schnaak, 1967; Seidler et al., 1970; Vonk, 1971) and nonbiological (Klöpping and Van der Kerk, 1951; Petrosi-

ni et al., 1963; Viel and Chancogne, 1971) alteration. It dissolves in water to the extent of 2 g/l. at 30° (Stecher, 1960) but, with the exception of methanol and ethanol, it has low to negligible solubility in common organic solvents. This water solubility helps to explain its lack of persistence as a foliage residue (Onley and Yip, 1971) and suggests that it might be found as an environmental contaminant in agricultural runoff waters. Because of the

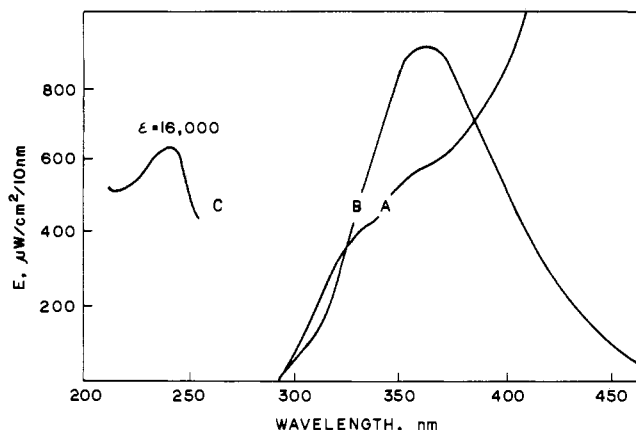Department of Environmental Toxicology, University of California, Davis, California 95616.

Figure 1. (A) The emission spectrum of sunlight; (B) the emission spectrum of an F40BL UV lamp; (C) absorption spectrum of ETU.

demonstrated photodecomposition of many chemicals in aqueous media (Crosby, 1972), we have investigated the effect of sunlight on low levels of ETU in water.

EXPERIMENTAL SECTION

Materials and Methods. Ethylenethiourea (Aldrich Chemical Co.) was recrystallized from ethanol, mp 197–98°. Other reagents and standards were commercial products used as received. N-(2,4-Dinitrophenyl)glycine was prepared by the method of Biserte et al. (1960).

Solutions of ETU (0.5–50 mg/l.) in deionized water were irradiated by exposure to summer sunlight (Davis, Calif.) in 4-l. Erlenmeyer flasks or to ultraviolet (uv) light in a laboratory photoreactor (Crosby and Tang, 1969) equipped with an F40BL lamp (General Electric Co., Schenectady, N. Y.). Photolysis was sensitized by acetone (5 ml/l.), riboflavin (10 mg/l.), rhodamin B (10 mg/l.), or methylene blue (10 mg/l.). Appropriate dark controls and sensitizer controls without ETU were included. Other compounds were irradiated in the same way.

Samples of agricultural drainage waters were collected from three sites in Yolo County, Calif., and used as collected and also boiled under reflux for 5 min prior to use. Filtered samples were fortified with ETU at 0.5 mg/l. before irradiation.

Isolation and Identification of Products. Irradiated solutions were concentrated on a rotating vacuum evaporator and subjected to thin-layer chromatography (tlc) on 20-cm square glass plates coated with silica gel F_{254} (0.25 mm) with chloroform–ethanol (90:5, v/v) (solvent A) or ethanol–butanol–water (77:48:5, v/v) (solvent B). Separated compounds were detected by their uv absorption after preparative tlc and more specifically with iodine vapor (ETU), 0.1% ninhydrin in 8% alcoholic acetic acid (glycine, hydantoin), or 1% p-(N,N-dimethylamino)benzaldehyde in ethanol-4 N hydrochloric acid (3:1) (ethyleneurea) as an aid to identification.

Elution of the compound moving at R_f 0.05 (solvent A) with ethanol and acetone, followed by centrifugation and evaporation, provided a white crystalline product which cochromatographed with authentic ethyleneurea: ir 5.95 (CO), 6.68 (CON), 6.92 (CH₂), 7.85 (CONHR), 9.1, 9.6, (C–OH) μ, identical with that of ethyleneurea.

Dilution of the concentrated photolyzate with acetone produced a precipitate which was collected by centrifugation; it formed a purple color with ninhydrin reagent, a white precipitate from aqueous solution with barium chloride, and remained at the origin on tlc: ir 8.90 (SO_4^{2-}), 6.20, 6.85 (COO⁻) μ.

An aqueous solution containing 0.5 mg/ml of this product was treated with 25% of its volume of saturated sodi-

um bicarbonate solution, and an equal volume of 2,4-dinitrofluorobenzene in methanol was added to provide at least a twofold molar excess of reagent. After 3 hr, the mixture was subjected to tlc (solvent A) and the band at R_f 0.29 was eluted as before to give yellow–orange crystals, R_f 0.29 (solvent A) and 0.72 (solvent B): ir 2.83 (NH), 3.40, 6.80 (CH₂), 6.22, 6.95 (COO⁻) μ; nmr (DMSO-d_6) δ 3.44 (CH₂). These properties were identical with those of authentic N-(2,4-dinitrophenyl)glycine.

Analysis. Aliquots of the irradiated solutions (300 ml) were evaporated to dryness and redissolved in methanol, the absorbance at 239 nm was measured with a Beckman DK-2 recording spectrophotometer, and analytical values were read from a standard curve prepared from pure ETU. Photolysis products did not interfere. Semiquantitative analysis of the agricultural water samples was accomplished by determining the dilution of irradiated sample required to reach the limit of visual detection of ETU on tlc (0.1–0.2 μg). Sulfate was determined gravimetrically by precipitation as the barium salt.

RESULTS AND DISCUSSION

The effective short-wavelength cutoff of sunlight is considered to be about 300 nm (Koller, 1965)(spectrum A, Figure 1); simulated sunlight in the laboratory provided spectrum B. As its wavelength of maximum absorbance lies at 240 nm, ETU does not absorb appreciable energy in the sunlight region (Curve C), and analysis by uv spectrophotometry (Figure 2) revealed no loss of ETU on irradiation in deionized water in either the laboratory photoreactor or Davis summer sunlight.

In the presence of a sensitizer, many otherwise inert compounds undergo photochemical reactions. Addition of acetone as a sensitizer resulted in the rapid disappearance of ETU under both natural and artificial light. For example, more than 95% was lost from a 0.64-ppm solution within 4 hr in the laboratory photoreactor (Figure 2).

Interruption of the acetone- or riboflavin-sensitized photolyses, while more than 50% of the ETU still remained, permitted the isolation of ethyleneurea (2-imidazolidone); repeated attempts to detect hydantoin (2,4-imidazolidinedione) were unsuccessful and, if present, it accounted for less than 5% of the original ETU. The product obtained by precipitation after less than 5% of the ETU remained was identified as glycine sulfate. Neither an irradiated solution of sensitizer nor the combined solutions of ETU and sensitizer kept in the dark gave the observed photoproducts.

Several other sensitizers were added at 10 ppm to a 25-ppm solution of ETU and exposed to sunlight. After 4
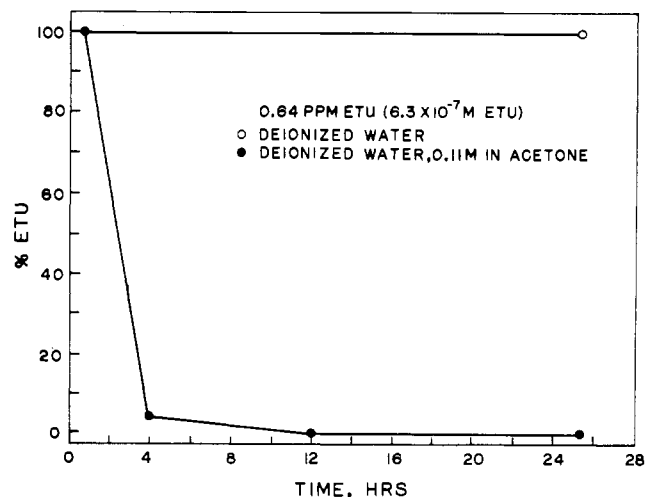

Figure 2. Rate of ETU photodecomposition in the presence and absence of acetone as sensitizer.

Table I. Photodecomposition of ETU in Agricultural Waters

Source	Irradiation	% ETU remaining
Irrigation ditch (sugar beet)	3 days, lamp	10–20
	3 days, dark	100
Paddy flooding ditch (rice)	24 days, sun	25–50
	24 days, dark	100
Paddy (rice)	24 days, sun	10–25
	24 days, dark	100

Figure 3. Proposed photodecomposition pathway of ETU in the presence of water and dissolved oxygen.

days with riboflavin as sensitizer, the concentration of ETU was less than 5% of that in the dark control; after 16 days, solutions with rhodamin B or methylene blue produced the same result. The reaction with riboflavin was repeated on a larger scale, and glycine was qualitatively identified as a photolysis product by its reaction with 2,4-dinitrofluorobenzene to form the expected derivative.

Sensitizers such as riboflavin and chlorophyll would be expected to occur in natural waters, and so the sensitized photolysis of ETU in the field seems entirely plausible. Natural interferences precluded spectrophotometric measurements, but semiquantitative tlc detected the slow photolysis of ETU upon irradiation of fortified agricultural drainage samples (Table I). To minimize microbial degradation, the procedure was repeated with each water sample after filtration and boiling for 5 min, with the same results. It is clear that decomposition in sunlight was more rapid than other nonbiological degradation in each instance.

We propose the pathway shown in Figure 3 for the sensitized photooxidation of ETU in sunlight. Cyclic thioureas are known to be oxidized to the corresponding ureas by nonphotochemical processes (Ware, 1950); ethyleneurea has been reported to be photooxidized to hydantoin (Ingamells, 1963) and, under our conditions of acetone-sensitized photolysis, ethyleneurea and hydantoin both produced glycine. Neither acetone nor riboflavin sensitized the photolysis of ETU when the irradiated solution was purged with N_2, so dissolved oxygen apparently is necessary for these reactions, perhaps in its excited singlet state (Schenck, 1969). With acetone as sensitizer, sulfate quantitatively accounted for the sulfur from decomposed ETU, but the glycine actually isolated in a typical experiment represented as little as 15% of the ETU lost. However, the photolysis of glycine is also a dynamic process; when irradiated alone under the same conditions, it decomposed to unknown products almost as rapidly as did ETU.

This research has demonstrated that the normally stable ETU undergoes sensitized photooxidation in sunlight to form inorganic sulfate and other oxidation products. Although the contribution of photodecomposition to the
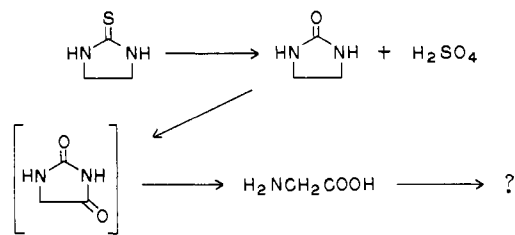
destruction of ETU was not measured directly in dithiocarbamate-treated fields, it is apparent that the possibility of such photodecomposition exists. Perhaps more important is the demonstration, for the first time, that agricultural waters can sensitize the photolysis of xenobiotics, and future investigations into the environmental photochemistry of pesticides and related products (e.g., for registration purposes) will have to consider the important influence of natural photosensitization.

ACKNOWLEDGMENT

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