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PHOTODEGRADATION OF PESTICIDES: PHOTOLYSIS OF 2-MERCAPTOBENZOTHIAZOLE AND 2-MERCAPTOBENZIMIDAZOLE[§]

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Abstract - Upon their application, organic pesticides are usually exposed to light under a variety of conditions. After some time, most of them undergo photodecomposition, especially in solution, and give degradation products with properties different from those of the original compounds. Thus, studies of the photochemistry of pesticides under controlled laboratory conditions are of interest. As an example, model studies of the photodegradation of 2-mercaptobenzothiazole (1, used as fungicide, bactericide, and disinfectant) and of the π-isoelectronic, biologically active 2-mercaptobenzimidazole (2) have been carried out. Uv irradiation of 1 in the presence of air oxygen in a pyrex flask yielded bis-(2-benzothiazolyl) disulfide when dry benzene or toluene were used as the reaction medium. With solutions of 1 in methanol, ethanol, or acetonitrile, the corresponding bis-(2-benzothiazolyl) disulfone was obtained as the intermediate, with benzothiazole sulfate as the final reaction product. Similarly, photolysis of 2 in methanol, ethanol, or acetonitrile yielded bis-(2-benzimidazolyl) disulfone and benzimidazole sulfate as the final product.

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INTRODUCTION

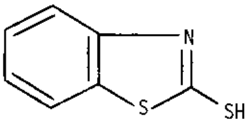
Chemical, microbial, and photochemical decomposition, adsorption, volatilization, movement, and organism uptake represent some of the important factors determining the fate of pesticides in soil and water systems.[1-5] Among these factors, photodecomposition of pesticides becomes especially important in areas with high insolation (exposure to sunlight) such as the arid and semi-arid U.S. Southwest and other arid and semi-arid regions throughout the world.

While irradiation of pesticides in the solid state has only limited effects, most pesticides undergo at least some photodecomposition in solution. Many commonly used pesticides (herbicides, fungicides, rodenticides, insecticides, bactericides, etc.) contain aromatic and/or heteroaromatic rings and, consequently, they absorb ultraviolet light. Their exposure to sunlight after their use in the environment can and usually will result in photodecomposition. While most of the photodegradation products normally do not pose any threat to higher organisms and humans, some of them can be toxic and potentially dangerous. Thus, photochemical studies of photodegradation of pesticides are of considerable interest.

Pesticides are normally exposed to sunlight under a variety of different conditions. During their application they are present in water droplets in the air which then come into contact with plant and soil surfaces. Volatile pesticides deposited on these surfaces may then be released back into the atmosphere, or they may penetrate into soil and contaminate surface and underground water.[2] This means that molecules of pesticides will interact with a number of various environmental components. Because of all these factors, environmental photochemistry of pesticides is a complex and difficult area of organic photochemistry.

On the other hand, in laboratory experiments, photodecomposition of pesticides can be studied under well-defined and controlled conditions. In the chemical literature, one can find the description of experiments carried out on solid supports (filter paper, aluminum plates, glass plates, soil surfaces), with solutions or suspensions of pesticides in water or organic solvents, and a few gas-phase studies.[2]

In this work, we have decided to study the photochemical behavior and decomposition of 2-mercaptobenzothiazole (1) and the π-isoelectronic 2-mercaptobenzimidazole (2) in the liquid phase, in a homogeneous solution. 2-Mercaptobenzothiazole (1) is used as a fungicide, bactericide, disinfectant, and wood preservative.[6-15] Also the related 2-mercaptobenzimidazole (2) is biologically active.[8,16-18] This investigation will serve as a starting point for a series of future studies of the photodecomposition of pesticides which we plan to carry out in our laboratories.



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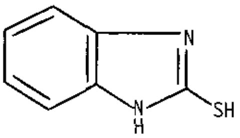

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RESULTS AND DISCUSSION

In recent years, there has been an increased interest in the photochemistry of heterocyclic compounds in general[19-23] and in the environmental photochemistry of heterocyclic pesticides in particular.[1-5]

However, there is no information available in the chemical literature concerning the photolysis of 2-mercaptobenzothiazole (1) and 2-mercaptobenzimidazole (2). It has been shown that one of the parent compounds, benzothiazole, undergoes photolysis in air-saturated acetonitrile and gives the benzothiazole dimer - 2,2'-bis-benzothiazole, in a 30% yield.[24] This reaction does not take place in water, methanol, ethanol, 2-propanol, or methylcyclohexane, and the mechanism appears to be rather complex. Similarly, uv irradiation of benzimidazole in ethanol resulted in the formation of two dimers, viz., 2,4'-bis-benzimidazole (16%) and 2,6'-bis-benzimidazole (25%) whereas the symmetrical 2,2'-bis-benzimidazole was not observed.[25] Also the π-isoelectronic benzoxazole and benzisoxazole have been reported to undergo photodehydrodimerization affording 2,2'-bis-benzoxazole.[24] Analogous photodehydrodimerizations of benzo[b]thiophene have been studied as well.[26,27] In our study, we have irradiated a solution of 2-mercaptobenzothiazole (1) in 96% air-saturated ethanol, methanol, or acetonitrile using a 450 W Hanovia mercury lamp and a pyrex well. The reaction can be easily followed by uv spectrometry (Figs. 1 and 2). After 22 h, the small amount of the yellowish-green precipitate was filtered off and identified as bis-(2-benzothiazolyl) disulfone (4a), on the basis of its ir spectrum and elemental analysis. The disulfone 4a had a molecular formula $C_{14}H_8N_2O_4S_4$ and exhibited absorption bands at 1160 and 1300 cm^{-1} in its ir spectrum (SO in SO_2).

Evaporation of the clear solution after filtration yielded the final product of the photolysis in an almost quantitative yield. The product, $C_7H_7NO_4S_2$, was identified as benzothiazole sulfate (5a), on the basis of its elemental analysis and the NMR, ir, uv, and mass spectral data. The NMR spectrum contained signals at δ 4.5 (2H, 2OH), 6.7-7.1 (4H, aromatic), and 8.6 ppm (1H, CH).

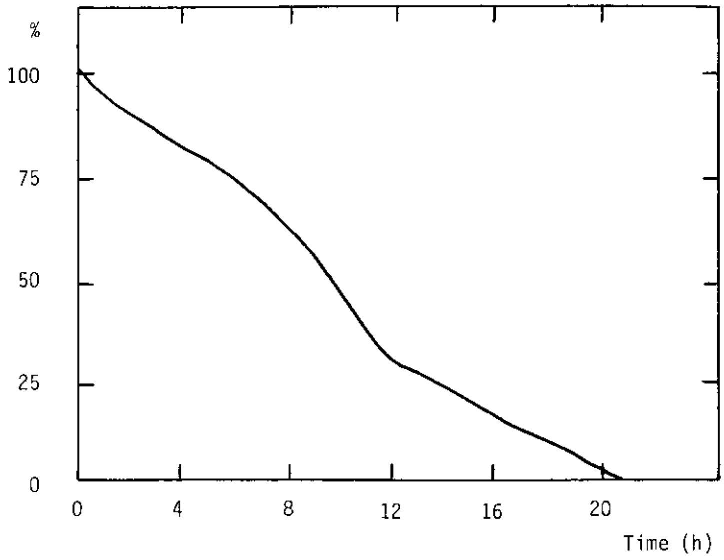


Fig. 1. Photodegradation rate of 7.7×10^{-3} M solution of 2-mercaptobenzothiazole (1) in 96% ethanol (followed at 320 nm).

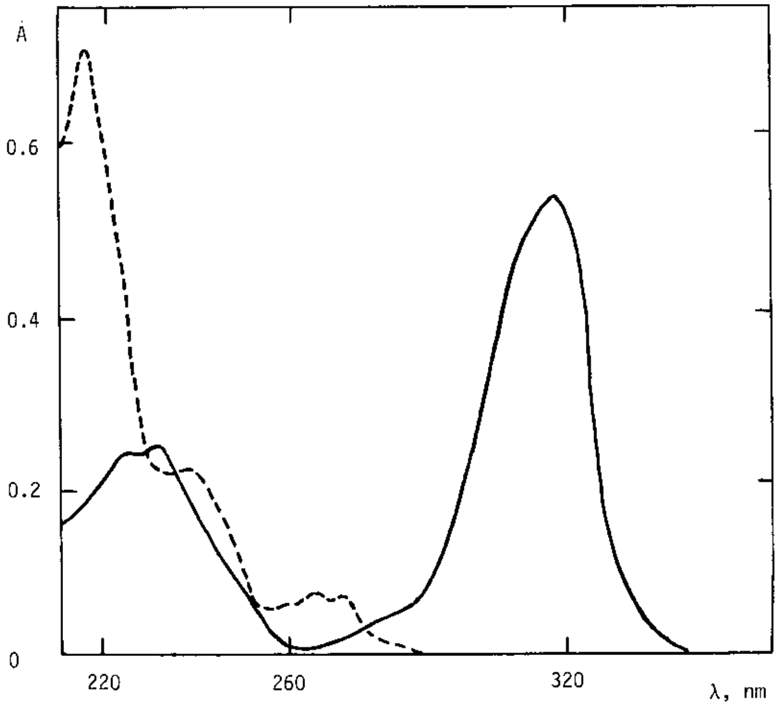
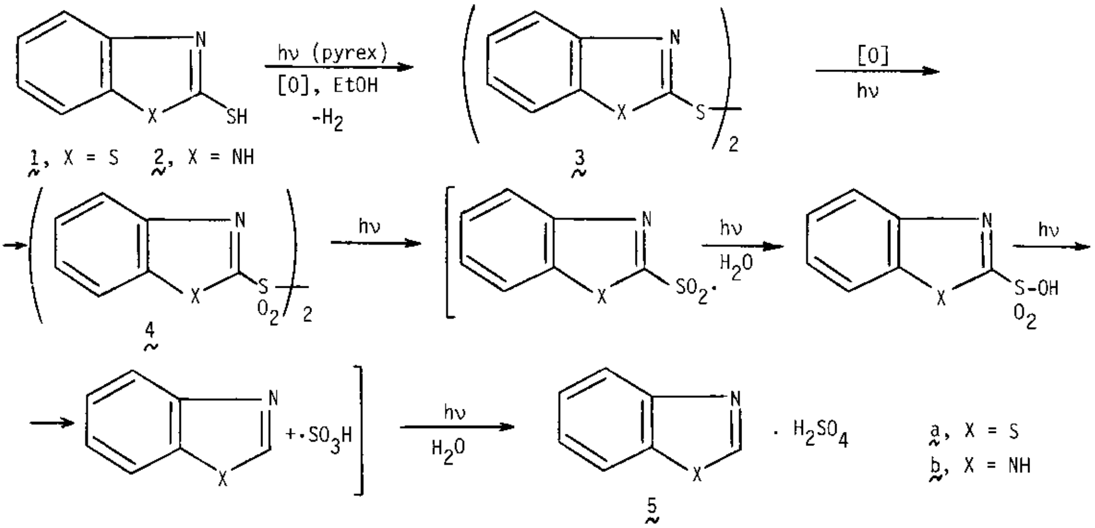


Fig 2. The uv spectrum of 10^{-5} M 2-mercaptobenzothiazole in ethanol (————); uv spectrum of the solution after photolysis (-----------).

After neutralization, the NMR spectrum of benzothiazole (the free base) measured in chloroform-d showed signals at δ 7.5-7.9 (4H, aromatic) and 9.1 ppm (1H, CH). The ir spectrum possessed bands at 3140-2850 (broad, OH), 1220, 1165, 1128, and 1010 cm^{-1} (organic sulfate). The uv spectrum exhibited absorption maxima at 212, 245, 280, and 290 nm, and was similar to that of the free benzothiazole. The mass spectrum showed peaks at m/e 135 and 108 corresponding to benzothiazole and the fragment after the loss of HCN. Also, benzothiazole sulfate (5a) was obtained when the disulfone 4a was irradiated for 10 h. When the reaction was carried out in dry benzene or toluene, the intermediate bis-(2-benzothiazolyl) disulfide (3a), $C_{14}H_8N_2S_4$, was identified as the major reaction product. Its spectral characteristics were in agreement with those reported in the literature, the compound was identical in all respects with an authentic sample of 3a synthesized by direct oxidation of 2-mercaptobenzothiazole (1) with hydrogen peroxide,[28] and there was no depression of the mixed melting point. No photodecomposition was observed when 2-mercaptobenzothiazole (1) was irradiated in absolute ethanol under nitrogen. This indicates that oxygen is necessary for the reaction to take place and that water is needed for the last steps of the reaction sequence (Scheme 1).



Scheme 1

Photolysis of 2-mercaptobenzothiazole (1) and 2-mercaptobenzimidazole (2)

On the basis of the isolated reaction products and intermediates, reaction conditions, and reaction mechanisms proposed in the literature for the photodecomposition of thiols,[27,29,30] it is likely that the mechanism of the photodecomposition corresponds to the one depicted in Scheme 1. We have also investigated the photolysis of 2-mercaptobenzimidazole (**2**) under conditions analogous to those described for 2-mercaptobenzothiazole (**1**). As expected, the major reaction product was benzimidazole sulfate (**5b**), $C_7H_8N_2O_4S$, identified by its mixed melting point with an authentic sample and the spectral data. Its ir spectrum possessed bands at 3150-2850 (broad, OH), 1525, 1460, 1380, 1360, 1340, 1260, 1220, 1180, and 1020 cm^{-1} (organic sulfate) and the uv absorption spectrum with the maxima at 216, 244, 267, and 267 nm resembles that of the free benzimidazole. When the irradiation was carried out in acetonitrile, the additional reaction product was bis-(2-benzimidazolyl) disulfone (**4b**), $C_{14}H_{10}N_4O_4S_2$, with elemental analysis corresponding to this molecular formula. No bis-(2-benzimidazolyl) disulfide (**3b**),[31] $C_{14}H_{10}N_4S_2$, was isolated after the photolysis of **2**. Again, we assume that the reaction proceeds according to the Scheme 1.

EXPERIMENTAL

Compounds. 2-Mercaptobenzothiazole and 2-mercaptobenzimidazole were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. All solvents used in this work were reagent grade. Absolute ethanol was obtained by dehydration with magnesium turnings.

Irradiations. An immersion-well type, water-cooled Ace Glass photochemical reactor (pyrex well, Hanovia 450 W mercury lamp) was used for all preparative irradiations (Ace Glass, Inc., Vineland, New Jersey).

Physical Constants and Spectral Data. All melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. The NMR spectra were obtained in deuterium oxide, ethanol-*d*$_6$, and chloroform-*d* on a Varian EM-360 spectrometer (60 MHz), with tetramethylsilane as the internal reference. The infrared spectra were measured in nujol on a Perkin-Elmer 580B spectrophotometer with a 3600 CDS data station. The electronic absorption spectra were recorded in ethanol using a Cary 118 spectrophotometer. The mass spectra were taken on a Perkin-Elmer RMu-6E spectrometer operating at 70 eV ionizing potential. Elemental microanalyses were carried out by MicAnal, Tuscon, Arizona, and by the Microanalytical Laboratory, University of Cairo, Giza, Egypt.

Photolysis of 2-Mercaptobenzothiazole (**1**)

A. Irradiation in Ethanol, Methanol, or Acetonitrile (in the presence of oxygen)

A solution of 2-mercaptobenzothiazole (**1**, 0.3 g, 0.0018 mole) in air-saturated 96% ethanol (350 ml) was placed in the photochemical reactor vessel (pyrex) and irradiated for 22 h. After irradiation, the reaction mixture was filtered and evaporated on a rotary evaporator under reduced pressure. The material separated from the irradiated solution by filtration was a small amount of yellowish-green bis-(2-benzothiazolyl) disulfone (**4a**, 0.035 g, 4%), m p > 360°C (dec.); ir spectrum (nujol): $\tilde{\nu}_{max}$ 1160, 1300 cm^{-1} (SO in SO_2). The compound is insoluble in organic solvents, mineral acids, and 10% aqueous sodium hydroxide.

Anal. $C_{14}H_8N_2O_4S_4$ (396.48) calcd. (found): N, 7.06 (7.29); S, 32.34 (32.47)%.

The solid obtained after evaporation was collected and recrystallized to give white crystals of benzothiazole sulfate (**5a**, 0.4 g, 95%), m p 157°C (ethyl acetate, lit.[32] m p 157-157.5°C); NMR spectrum (ethanol-d_6): δ 4.5 (2OH), 6.7-7.1 (4H, aromatic), 8.6 ppm (1H, heterocyclic CH) (for comparison, see the NMR spectrum of benzothiazole in dimethyl sulfoxide-d_6[33]); ir spectrum (nujol): $\tilde{\nu}_{max}$ 3140-3250 (broad, OH), 1220, 1165, 1128, 1010 cm^{-1} (organic sulfate) (for the ir spectrum of benzothiazole - neat - see ref.[34]); uv spectrum (ethanol): λ_{max} (log ε), 212 (4.85), 245 (4.30), 280 (3.70), 290 nm (3.54) [for benzothiazole in ethanol, lit.[35] gives the following main adsorption maxima: λ_{max} (log ε) 217 (4.30), 252 (3.78), 285 (3.25), 294 (3.16), 324 nm (1.53)]; mass spectrum, main peaks at m/e 135 (base peak, 100%, benzothiazole), 108 (78%, benzothiazole - HCN).

Anal. $C_7H_7NO_4S_2$ (233.26) calcd. (found): C, 36.04 (35.86); H, 3.02 (2.75); N, 6.00 (5.90); S, 27.49 (27.60) %. The same results were obtained with methanol or acetonitrile as the solvent.

B. Irradiation in Benzene or Toluene (in the presence of oxygen)

Irradiation of 2-mercaptobenzothiazole (**1**) under the conditions described above (under A) but with benzene or toluene as the solvent yielded bis-(2-benzothiazolyl) disulfide (**3a**) as the main reaction product; white crystals, m p 178-180°C (from acetic acid, lit.[28] m p 179-180°C). The compound was identical in all respects with an authentic sample of **3a** synthesized by the procedure described below. The mixed melting point showed no depression.

C. Irradiation in Ethanol (degassed solution)

2-Mercaptobenzothiazole (**1**) in absolute ethanol was irradiated for 30 h by using the same procedure as described in A but with nitrogen gas constantly bubbled through the solution. The solvent was then evaporated on a rotary evaporator under reduced pressure. The starting material (**1**) was recovered without any loss in weight. No photodegradation took place.

Synthesis of Authentic Bis-(2-benzothiazolyl) Disulfide (3a)

2-Mercaptobenzothiazole (**1**, 1.0 g, 0.060 mole) was dissolved in ethanol (50 ml) and 30% aqueous hydrogen peroxide (3.5 ml, 0.031 mole) was added to the solution with stirring during a period of 10 min. The precipitated solid was collected and recrystallized to give an almost quantitative yield of bis-(2-benzothiazolyl) disulfide (**3a**), m p 179-180°C (acetic acid, lit.[28] m p 179-180°C). For a mass spectrum of **3a**, see ref.[36]; for the ir spectrum in KBr disk, ref.[37]

Photolysis of 2-Mercaptobenzimidazole (**2**)

Irradiation of 2-mercaptobenzimidazole (**2**) in ethanol, methanol, or acetonitrile was carried out in the same manner as described for 2-mercaptobenzothiazole, with the same amounts and comparable yields of products. The main product formed as the result of irradiation was benzimidazole sulfate (**5b**), white crystals, m p 180-181°C (from ethanol-diethyl ether); picrate of the free base, yellow crystals, m p 223°C (lit.[38] m p 220°C). No depression of the melting point with an authentic sample of benzimidazole sulfate; ir spectrum (nujol); $\tilde{\nu}_{max}$ 3150-2850 (broad, OH), 1525, 1460, 1380, 1360, 1340, 1260, 1220, 1180, 1020 cm^{-1} (organic sulfate) (for the ir spectrum of benzimidazole in KBr disk - see ref.[39]); uv spectrum (ethanol): λ_{max} (log ε): 216 (4.23), 244 (4.20), 267 (3.85), 274 nm (3.95) [for benzimidazole in ethanol, lit.[40] gives λ_{max} (log ε): 244 (3.74), 272 (3.71), 279 nm (3.73)].

With acetonitrile as the solvent, the additional product isolated from the reaction mixture was bis-(2-benzimidazolyl) disulfone (**4b**), m.p. 275°C (dec.).

Anal. $C_{14}H_{10}N_4O_4S_2$ (362.39) calcd. (found): C, 46.40 (45.8); H, 2.78 (3.1); N, 15.46 (15.6); S, 17.70 (18.2)%.

No bis-(2-benzimidazolyl) disulfide was isolated from the reaction mixture.[31]

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