

Ultraviolet Irradiation of an Aqueous Solution of Prometryn in the Presence of Humic Materials

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UV irradiation of prometryn [2-(methylthio)-4,6-bis(isopropylamino)-s-triazine] at 253.7 nm in distilled water and humic acid suspension (pH 3) produced a reaction having a first-order reaction rate. However, second-order reaction rate kinetics was observed in the presence of dissolved humic acid (pH 6 and 8) and fulvic acid (pH 3, 6, and 8). Irradiation of prometryn in the absence of dissolved humic material resulted in the formation of 2-hydroxy-4,6-bis(isopropylamino)-s-triazine and 4,6-bis(isopropylamino)-s-triazine. An additional dealkylated product [4-amino-6-(isopropylamino)-s-triazine] was formed when the photolysis of prometryn was performed in aqueous solutions of humic acid or fulvic acid. It is suggested that the hydroxyl radicals generated during UV irradiation of aqueous solution of humic materials dealkylated the 2-H analogue of prometryn.

Environmental relevance of photodegradation of pesticides with a sensitizer has been reported in several recent papers. Photosensitization of pesticides with model compounds, such as benzophenone (Plimmer and Kearney, 1969), riboflavin (Rosen et al., 1970; Ross and Crosby, 1973), acetone (Ross and Crosby, 1973; Burkhard and Guth, 1976), and dye (Acher and Saltzman, 1980; Acher and Dunkelblum, 1979) have been observed although the occurrence of these compounds is unlikely under natural environmental conditions. Many surface waters and soil solutions contain organic materials, such as humic substances, that strongly absorb light. These materials may sensitize the photodegradation of pesticides by several indirect processes (Crosby, 1970). Humic materials and dissolved organic substances in natural and agricultural waters have been shown to sensitize the photolysis of atrazine (Kahn and Schnitzer, 1978), ethylenethiourea (Ross and Crosby, 1973), sustar (Miller and Crosby, 1978), and 3,4-dichloroaniline (Miller et al., 1980). Photosensitization may be caused by hydrogen abstraction, by oxidation with superoxide, hydrogen peroxide, hydroxyl radicals, or singlet oxygen, or by reaction with other photochemically generated intermediates (Miller et al., 1980).

The objective of this study was to investigate the influence of humic materials on the rate and route of photodegradation of prometryn [2-(methylthio)-4,6-bis(isopropylamino)-s-triazine] when exposed to UV irradiation. It was thought that the results of this study may demonstrate the importance of indirect processes initiated by naturally occurring organic material when assessing the photolysis of synthetic chemicals in aqueous solutions.

EXPERIMENTAL SECTION

Humic Materials. *Fulvic Acid (FA).* The FA originated from the Bh horizon of a Podzol soil in Prince Edward Island, Canada. Methods of extraction and purification were the same as those described by Schnitzer and Skinner (1968). The purified FA, which constituted about 75% of the total organic matter in the soil sample, contained 1.0% ash and, on a moisture and ash-free basis, 50.9, 3.3, 0.7, 0.3, and 44.7% C, H, N, S, and O, respectively. Functional group analysis showed 5.0, 3.3, 3.6, 0.6, 2.5, and 0.1 mequiv/g COOH, phenolic OH, alcoholic OH, quinonoid C=O, and OCH₃ groups, respectively (Schnitzer and

Skinner, 1968; Gamble, 1972).

Humic Acid (HA). The HA originated from a soil sample that was taken from the undisturbed Ah horizon of a Black Chernozem soil in Alberta, Canada. Methods of extraction, separation, and purification of the HA were identical with those described elsewhere (Khan, 1971). The purified HA contained 0.7% ash, and on moisture and ash-free basis 54.4, 5.5, 4.1, 1.1, and 33.0% C, H, N, S, and O, respectively. Functional group analysis showed 4.5, 2.1, 2.8, 4.5, and 0.3 mequiv/g of COOH, phenolic OH, alcoholic OH, C=O, and OCH₃ groups, respectively. The extracted and purified HA accounted for 28% of the organic matter in the original soil sample (Khan, 1971).

Chemicals. All solvents were of pesticide grade and used as received. Authentic samples of prometryn and metabolites were a gift from Ciba-Geigy, Ltd., Switzerland.

Photochemical Procedure. The photochemical reaction vessel was equipped with an outer condenser and a magnetic stirring bar. Solution temperature was maintained at 23 °C by circulating water through a condenser with a thermostatic Haak Model FJ water bath. The light source was a UV Pen Ray lamp (Model II, SC-IL, 5.5 W, manufactured by Ultraviolet Products, Inc., San Gabriel, CA) with the 253.7-nm line comprising 92% of the total irradiation. The Pen Ray lamp was inserted snugly into the solution through the neck of the vessel. Photometric absorbance measurements at 253.7 nm were made on 1/10 dilutions of the experimental solutions. For a 1-cm path length, the photometric absorbances of the undiluted solutions of prometryn, FA, and HA were 0.7, 5.3 and 6.3, respectively.

In the photolysis experiment, 2.1×10^{-4} M prometryn solution in distilled water or 0.05% (w/v) FA or HA solutions in distilled water containing prometryn (2.1×10^{-4} M) at pHs 3.0, 6.0, and 8.0 were irradiated for various lengths of time. The pH of the solution was adjusted with either dilute HCl or NaOH. The pH of 0.05% FA and HA solution in distilled water was ~2.9-3.0. Kinetics of the photolysis was followed by measuring the residual concentrations of prometryn remaining in solution at known time intervals. In all cases, dark controls were run at the same pHs and concentrations as those of the corresponding photolysis.

Analytical Procedures. *Determination of Prometryn.* An aliquot (0.5 mL) of the irradiated solution taken at selected time intervals was taken to dryness under reduced pressure at room temperature and the residue dissolved in methanol. An aliquot of this solution was analyzed for prometryn by gas chromatography (GC).

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Identification of Photolysis Products. Irradiated solution taken at the termination of the experiment was evaporated by dryness under reduced pressure at room temperature. The residue was dissolved in a small volume of methanol and a portion of the solution was subjected to thin-layer chromatography (TLC). To the remaining methanolic solution, an excess of freshly prepared diazomethane solution was added and then allowed to stand with occasional shaking at room temperature for about 3 h. The mixture was taken to dryness with a stream of dry air, and the residue was dissolved in methanol and subjected to TLC. Compounds separated by preparative TLC were eluted with methanol, reduced to a small volume, and analyzed by GC. Fractions obtained from TLC of unmethylated material as described above were also methylated or ethylated before GC analysis. Ethylation was achieved by dissolving the dried material in a small volume of ethyl acetate and by adding to it an excess of freshly prepared ethereal diazoethane solution. The mixture was allowed to stand with occasional shaking at room temperature for about 1 h, excess of the reagent was removed, and the residual solution was diluted with ethyl acetate and analyzed by GC.

Gas Chromatography (GC). The gas chromatograph was a Pye, series 104, Model 64, fitted with an alkali flame ionization detector having an RbCl annulus. The column used was a 1.5 m \times 0.4 cm i.d. glass tube packed with 3% Carbowax 20 M coated on 80–100-mesh Chromosorb WHP. On-column injections were used; the injector port temperature control was turned off; column and detector temperatures were 175 and 290 °C, respectively. The carrier gas (nitrogen), hydrogen, and air flow rates were 45, 35, and 300 mL/min, respectively.

Thin-Layer Chromatography (TLC). Precoated analytical plates of silica gel with fluorescent indicator (Eastman Chromagram Sheet) were used for TLC. The solvent system was acetone–hexane (7:3) and hexane–acetone (7:3) for unmethylated and methylated material, respectively. The plates were visualized under UV light.

Confirmation. The identity of the compounds was confirmed by comparing the TLC R_f values and GC retention times with those of authentic samples, by cochromatography, and finally by gas chromatography–mass spectrometry. A high-resolution mass spectrometer, Model VG 2AB-2F, connected to a Varian GC Model 3700 was used. The mass spectra were recorded at 70 eV.

RESULTS AND DISCUSSION

Kinetic Studies. Typical photolysis of prometryn at pH 6.0 with increasing time of exposure to UV irradiation is graphically presented in Figure 1. The degradation curves demonstrate that the photolysis of prometryn in aqueous solution was slower in the presence of FA or HA than in their absence. This indicates that humic materials absorbed most of the photons emitted from UV irradiation, thereby slowing down any direct photochemical reaction of prometryn. The absorbances of aqueous solutions of prometryn and humic materials diluted by a factor of 10 were as follows: 0.07; FA, 0.53; HA, 0.63. The humic material itself undergoes photochemical reactions forming products that may then react with the herbicide or its photolysis products (Chen et al., 1978; Khan and Schnitzer, 1978).

First-order kinetic behavior was observed for the photolysis of prometryn in water alone (Table I). The data at pH 6.0 and pH 8.0 suggest that the apparent first-order rate constants increased with increasing pH. The rate constant obtained at pH 3.0 may not be compared directly with those of pH values at 6.0 and 8.0, as it likely repre-

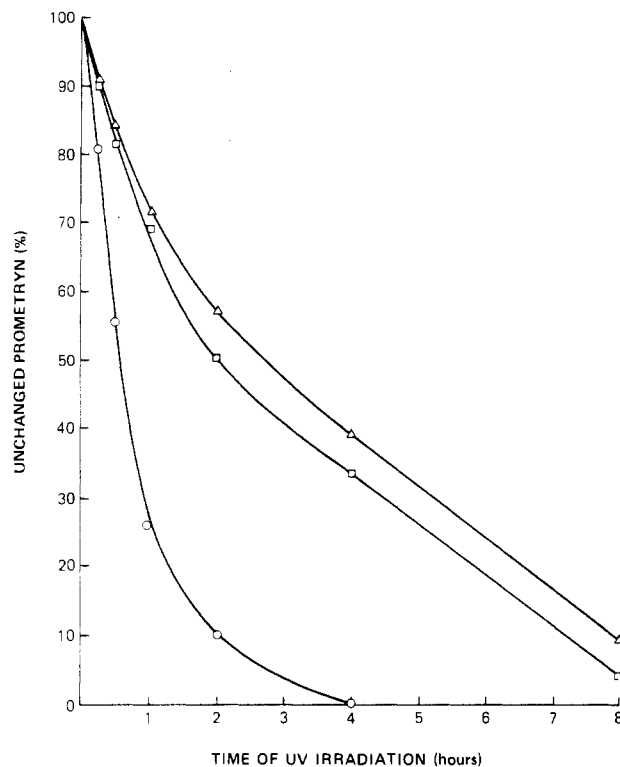


Figure 1. Effect of UV irradiation on prometryn (2.1×10^{-4} M) in the presence and absence of humic materials at pH 6.0. (○) Distilled water; (□) 0.05% aqueous solution of fulvic acid; (△) 0.05% aqueous solution of humic acid.

Table I. Apparent First-Order Rate Constant (k') and Half-Life ($t_{1/2}$) for the Photolysis of Prometryn^a at 23 °C

pH	k' , $\text{min}^{-1} \times 10^2$	$t_{1/2}$, min
Prometryn in Water		
3.0	2.25	30.8
6.0	1.97	35.2
8.0	3.41	20.3
Prometryn in 0.05% Aqueous Suspension of HA		
3.0	1.68	41.1

^a Initial concentration of prometryn (C_a^0) = 2.1×10^{-4} M.

sents singly protonated prometryn. Unprotonated prometryn is expected to exist only at the higher pH values ($\text{p}K_a = 3.05$).

The photolysis of prometryn in the presence of HA at pH 3.0 also followed the first-order kinetics (Table I). At this pH, the HA was insoluble and the suspended particles screened out only a limited amount of light by absorbance and Rayleigh scattering. Although under these conditions prometryn received a smaller UV irradiation flux, the photochemical processes qualitatively resembled those in water alone. The presence of suspended HA particles caused a decrease in the first-order rate constant (Table I).

In the photolysis of aqueous solutions of prometryn and dissolved HA (pH 6 and 8) or FA (pH 3, 6, and 8) having different initial concentrations, the reaction can be represented as



where A and B represent the reactant prometryn and the collection of photochemically activated species in the humic material, respectively. In this case, prometryn is screened from almost all of the light by the dissolved humic material. Thus, the total concentration of photochemically

activated species available for reaction will be the maximum obtainable for the light flux used.

The standard differential rate law for second-order kinetics was used for developing the necessary calculations procedure. Let C_a^0 be the initial concentration of prometryn and C_b^0 be the initial total concentration of all the photochemically activated species in the humic material. For the most general case in which $C_a^0 \neq C_b^0$, the differential and integral rate laws are (Laidler, 1950)

$$\frac{dM_x}{dt} = k(C_a^0 - M_x)(C_b^0 - M_x) \quad (2)$$

$$\frac{1}{(C_a^0 - C_b^0)} \ln \frac{C_b^0(C_a^0 - M_x)}{C_a^0(C_b^0 - M_x)} = kt \quad (3)$$

where M_x represents the molarity of the rate-determining reactant that is utilized during time t of the reaction and k is the rate constant. It is assumed that 1 mol of A (prometryn) reacts with 1 mol of B (photochemically activated species in the humic material) during photolysis. Since the nature of photochemically activated species in the humic materials is unknown and their concentration cannot be measured directly, the two unknowns, C_b^0 and k , in eq 2 and 3 must both be calculated from the differential rate law. Equation 2 can be written as

$$\frac{1}{C_a^0 - M_x} \frac{dM_x}{dt} = k(C_b^0 - M_x) \quad (4)$$

but

$$\frac{d(C_a^0 - M_x)}{(C_a^0 - M_x)dt} = -\frac{1}{(C_a^0 - M_x)} \frac{dM_x}{dt} = \frac{d \ln (C_a^0 - M_x)}{dt} \quad (5)$$

then

$$\frac{d \ln (C_a^0 - M_x)}{dt} = k(C_b^0 - M_x) \quad (6)$$

let

$$\frac{d \ln (C_a^0 - M_x)}{dt} = r \quad (7)$$

therefore

$$r = -kC_b^0 + kM_x \quad (8)$$

In the most general case that is possible, a collection of photochemically activated humic species could include reactants having different rate constants. If these rate constants were to have a large spread in their numerical values, then different humic reactant species would dominate at each stage of the reaction. The early part of the reaction would tend to reflect the faster rate constants, while the last part of it would be influenced by the slower rate constants. Under these conditions, the experimentally observed rate constant, k , would systematically decrease throughout the reaction. This would cause the r vs. M_x curve plotted according to eq 8 to have a decreasingly negative slope. The curve would have a concave shape. Whether or not this exists in any degree is unknown at this time. However, our present experiments were unable to detect anything more complicated than a straight line with a negative slope. The data showing apparent second-order behavior were therefore fitted to a straight line according to eq 9

$$r = C_0 + C_1M_x \quad (9)$$

where $C_0 = kC_b^0$ and $C_1 = k$.

Table II. Second-Order Rate Constant (k), Half-Life ($t_{1/2}$), and Total Concentration of Photoactive Reaction Species of Humic Materials for the Photolysis of Prometryn^a at 23 °C (Relative Standard Deviation $\pm 10\%$)

pH	$k, \frac{L}{M_x^{-1} \text{ min}^{-1}}$	$C_b^0, {}^b M, \times 10^4$	$t_{1/2}, \text{ min}$		$C_a^0 - M_x, {}^c M, \times 10^4$	
			theor	exptl	theor	exptl
Prometryn in 0.05% Aqueous FA Solutions						
3.0	57.36	2.14	80.7	85.8	1.09	1.09
6.0	33.24	2.24	130.3	120.0	1.19	1.18
8.0	27.90	3.02	103.7	97.2	1.97	1.94
Prometryn in 0.05% Aqueous HA Solutions						
6.0	27.96	2.28	151.0	163.2	1.23	1.24
8.0	19.08	2.67	178.3	173.3	1.62	1.61

^a Initial concentration of prometryn (C_a^0) = 2.1×10^{-4} M.

^b Initial total concentration of photoactive reactive species in humic material estimated from eq 9 ($\pm 10\%$).

^c Total concentration of photochemically reactive species remaining at $t_{1/2}$ (i.e., when $C_a^0 - M_x = 0.5C_a^0$).

The second-order rate constant and the initial total concentration of the photochemically activated species in the humic material was calculated from the least-squares fit of the straight line (eq 9).

The calculated values of the second-order rate constants are shown in Table II. In contrast to the first-order rate constants obtained in the absence of dissolved humic materials (Table I), the values of the second-order rate constants at pHs 6 and 8 decreased with increasing pH. Thus, it is apparent that different photolysis mechanisms existed in the absence and presence of dissolved humic materials.

It can be deduced from the known photometric absorbances that the dissolved humic material absorbs most of the incident radiation. The total photometric absorbance of a sample containing prometryn and a humic material in solution is given by eq 10.

$$A_T = A_1 + A_2 = -\log (I_T/I_0) \quad (10)$$

With the conventional 1-cm² cross section and 1-cm path length, A_1 and A_2 are the photometric absorbances of prometryn and of dissolved humic material at 253.7 nm and I_0 and I_T are the incident and transmitted energies for the whole sample. By rearranging eq 10 the amounts of energy transmitted by the whole sample, prometryn, and humic material can be obtained from eq 11, 12, and 13, respectively. In eq 11 and 12, the prometryn expression

$$I_T = 10^{-A_1}(10^{-A_2})I_0 \quad (11)$$

$$I_1 = I_T/10^{-A_2} = 10^{-A_1}I_0 \quad (12)$$

$$I_2 = I_T/10^{-A_1} = 10^{-A_2}I_0 \quad (13)$$

10^{-A_1} is a coefficient that will attenuate the energy otherwise transmitted by the sample. According to eq 12 for a solution of prometryn only, it will attenuate the energy I_0 . However, in accordance to eq 11 for a solution of both prometryn and humic material, the expression 10^{-A_1} will attenuate the much smaller energy $10^{-A_2}I_0$, otherwise transmitted by the humic solution. The energy absorbed by prometryn will correspond exactly to the attenuation that it will cause. Thus, if prometryn will attenuate the large quantity I_0 , it will absorb a large amount of energy. Similarly, if it attenuates the very small quantity $10^{-A_2}I_0$, then prometryn will absorb a very small amount of energy. The energy absorbed by prometryn must therefore be calculated for the two humic solutions, without and with prometryn. For example, when the FA solution was used

Table III. Mole Percent of the Photoactive Reactive Species of Humic Material in the Photolysis of Prometryn

pH	mol % reacted ^a
Prometryn in 0.05% Aqueous FA Solutions	
3.0	50.9
6.0	53.1
8.0	65.2
Prometryn in 0.05% Aqueous HA Solutions	
6.0	53.9
8.0	60.7

^a Mole percent of reacted species of humic materials when prometryn is 50 mol % reacted, i.e., $(C_b^0 - \frac{1}{2}C_a^0)/C_b^0 \times 100$.

with or without prometryn, eq 13 and 11 can be used to determine the energy absorbed $(\Delta E)_1$ by prometryn. Thus

$$(\Delta E)_1 = (I_2 - I_T) = (4.08 \times 10^{-6})I_0 \quad (14)$$

By parallel logic the energy absorbed $(\Delta E)_2$ by FA can be determined by using eq 12 and 11.

$$(\Delta E)_2 = (I_1 - I_T) = (1.86 \times 10^{-1})I_0 \quad (15)$$

Thus, the amount of energy absorbed by prometryn is about 5 orders of magnitude smaller than that absorbed by the fulvic acid. The comparison would be even more extreme for the HA solution. The amount of light absorbed by the prometryn is negligible compared with experimental error. In view of the foregoing, the assumption of total screening of prometryn from the light by the humic solutes under our experimental conditions is therefore a valid approximation upon which we have based the kinetics calculations.

Chen et al. (1978) reported that UV light caused the color of a FA solution to fade. It was observed that a 0.01% FA solution exposed to UV irradiation became colorless after 14, 11, and 9 h at pHs 3.5, 7.0, and 11.0, respectively. In our experiments, the absorbance of 0.05% FA and HA solutions measured at 465 nm also decreased with increasing time of exposure to UV irradiation. Thus, up to a period when 50% of the initially added prometryn was lost by UV irradiation, a 12% and 2% decrease in absorbance of FA and HA, respectively was also observed. This decrease in absorbance due to UV irradiation (loss of humic chromophores) should not be confused with the photochemically activated species of humic materials present during photolysis. Table III shows the mole percent of the reacted species of humic materials when 50 mol % of prometryn had reacted during the photolysis reaction. It was assumed that 1 mol of prometryn reacted with 1 mol of photochemically activated species in the humic material. Thus, it is obvious that the amount of the humic chromophores that apparently reacted is disproportionately small, compared with the amount of the photochemically activated species B that has reacted. Furthermore, the distinction between the two is greater with the HA than with the FA. These observations indicate that the photochemically activated species of the humic material and the humic chromophore are not chemically identical.

The half-life ($t_{1/2}$) of prometryn in water alone or in aqueous suspension of HA at pH 3.0 was calculated in the usual way from the first-order rate constant, i.e., $t_{1/2} = 0.693/k'$, where k' is the first-order rate constant (Table I). The $t_{1/2}$ values of prometryn in aqueous solutions of FA at pHs 3.0, 6.0, and 8.0 and of HA at pHs 6.0 and 8.0 were obtained as follows.

Equation 4 can be rearranged for the calculation of $t_{1/2}$ of prometryn. Thus, it follows that

$$t_{1/2} = \frac{1}{k(C_a^0 - C_b^0)} \left(\ln \frac{C_a^0 - M_x}{C_a^0} - \ln \frac{C_b^0 - M_x}{C_b^0} \right)$$

For $t_{1/2}$

$$\frac{C_a^0 - M_x}{C_a^0} = 0.5$$

$$t_{1/2} = \frac{1}{k(C_a^0 - C_b^0)} \left(\ln 0.5 - \ln \frac{C_b^0 - M_x}{C_b^0} \right) \quad (16)$$

The calculation of $t_{1/2}$ for prometryn requires numerical values of C_b^0 and $C_b^0 - M_x$, the initial time-dependent values of the photoactivated humic reactant (B) concentration. At this time the identity of B is unknown, and experimental values of C_b^0 and $C_b^0 - M_x$ are not available; our theoretical estimates of C_b^0 have, however, been tabulated in Table II. The use of this reaction scheme is based on the assumption that 1 mol of B reacts with 1 mol of A, thereby permitting a trial calculation of $t_{1/2}$. At the same time, experimental values of $t_{1/2}$ may be interpolated from the data in Table II. This should permit $C_b^0 - M_x$ to be estimated from eq 16. Our assumption appears to be correct as an internally self-consistent set of theoretical and experimental values were obtained for $t_{1/2}$ and $C_b^0 - M_x$ as shown in Table II.

An examination of Table II shows that for fulvic acid solutions, an increase of pH from 6.0 to 8.9 caused the rate constant and the half-life both to decrease. Furthermore, the initial total concentration, C_b^0 increased substantially in the same pH range. When the question about a simultaneous decrease in both the rate constant and the half-life is considered, two important points must be noted. The first is a fundamental difference in the mathematical properties of first-order and second-order kinetics. With first-order kinetics, the half-life is a function of only one parameter. It varies inversely with the rate constant. In contrast to this, in second-order kinetics the half-life depends on the three parameters k , C_a^0 , and C_b^0 . A decrease in k will result in an increase in half-life only if C_b^0 and C_b^0 are constant. If a decrease in the rate constant is accompanied by a sufficiently large increase in C_b^0 , then the half-life may also decrease. The second point is that the form of the second-order rate law based on $C_a^0 = C_b^0$ would be unable to properly detect and explain the result found here.

The data in Tables I and II demonstrate that under the experimental conditions described, the half-life of prometryn in distilled water or soluble FA solution was lengthened only at pH 6.0. However, in the presence of HA an increase in half-life of prometryn with an increase in pH was observed. Samples kept in the dark for a period up to 12 h showed no measurable decrease in the initial concentration of prometryn.

Photolysis Products. TLC of the photoproducts formed by UV irradiation of prometryn showed distinct spots with different R_f values (Table IV). These spots were scraped from the preparative TLC plates, eluted with methanol, and analyzed by GC. Photolysis of prometryn in water or in aqueous suspension of HA (pH 3.0) resulted in the formation of two products, II and III, having GC retention times of 3.5 and 9.6 min, respectively (Table IV). The concentration of III in the irradiated solution at the termination of experiment was considerably greater (>75%) than II. The presence of II was also confirmed by GC of the ethylated material from the origin of TLC plates of unmethylated material (Table IV). UV irradiation of prometryn in FA or HA solution showed the

Table IV. Thin-Layer Chromatography (TLC) and Gas Chromatography (GC) Data for Prometryn Photolysis Products

photolysis solvent system	unmethylated			methylated		
	TLC R_f value ^a	GC retention time, min	product ^d	TLC R_f value ^b	GC retention time, min	product
water and 0.05% HA suspension (pH 3.0)	0.00	9.6 ^c	II	0.00		
	0.50	3.5	III	0.17	3.5	III
0.05% FA and HA solution				0.44	9.6	II
	0.00	9.6 ^c	II	0.00		
	0.50	3.5	III	0.17	3.5	III
					4.2	IV
		0.92	20.2	I	0.44	9.6
				0.66	20.3	I

^a Acetone-hexane (7:3). ^b Acetone-hexane (3:7). ^c Methylated before analyzing by GC. ^d (I) prometryn; (II) 2-hydroxy-4,6-bis(isopropylamino)-s-triazine; (III) 4,6-bis(isopropylamino)-s-triazine; (IV) 4-amino-6-(isopropylamino)-s-triazine.

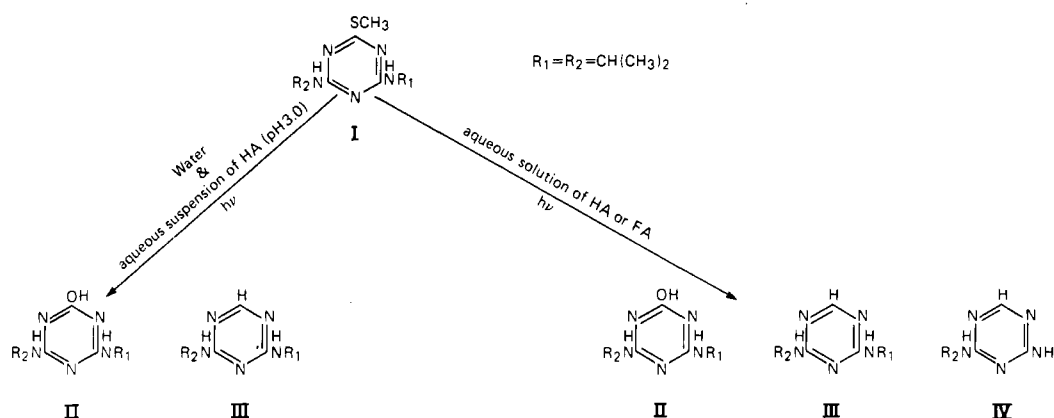


Figure 2. Compounds present in solution after UV irradiation of prometryn in the presence and absence of humic materials.

presence of an additional compound (IV) at a retention time of 4.2 min (Table IV). Furthermore, small amounts of prometryn (I) were also present in the irradiated solutions containing FA or HA. It should be noted that in the absence of soluble humic material, the TLC spots at R_f values of 0.50 and 0.17 resulted from unmethylated and methylated materials, respectively, gave only one GC peak with a retention time of 3.5 min. However, the spots at the same R_f values resulted from the material obtained by UV irradiation in the presence of soluble FA or HA gave an additional GC peak having a retention time of 4.2 min (Table IV). Thus, the material represented by the two GC peaks with retention times of 3.5 and 4.2 min was not chromatographically distinct on the TLC plates. The TLC spots and the GC peaks observed after UV irradiation had similar R_f values and retention times regardless of pH. In our experiments no attempt was made to quantitatively analyze photoproducts. TLC of the irradiated samples before GC analysis removed most of interfering material.

The identities of the photolysis products represented by the GC peaks (Table IV) were confirmed by cochromatography with authentic standards and finally by GC-MS analysis. The predominant ions in the mass spectra of materials represented GC peaks were $P - CH_3$, $P - C_3H_6$ and/or $P - (C_3H_6 + SCH_3)$ with further fragmentation analogous to the spectra obtained for authentic samples. Material represented by GC peaks with retention times 3.5 and 4.2 min (compounds III and IV) showed strong parent peaks 46 mass units below the molecular ion of prometryn and mono-N-dealkylated prometryn, respectively. The elimination of the C-2 sulfur atom of the $-SCH_3$ substituent with a mass decrease of 46 is an indication of hydrogen substitution. Thus, GC and GC-MS analysis of the compounds represented by peaks at retention times 3.5, 4.2, 9.6, and 20.2 min were identified as

4,6-bis(isopropylamino)-s-triazine (III), 4-amino-6-(isopropylamino)-s-triazine (IV), prometryn (I), and prometryn (II), respectively. Formation of III by irradiation of I has been also demonstrated by other workers (Plimmer et al., 1969; Pape and Zabik, 1970). In addition to the photoproducts formed by UV irradiation of prometryn in presence of dissolved HA and FA shown in Figure 2, a trace amount of the mono-N-dealkylated analogue of II [2-hydroxy-4-amino-6-(isopropylamino)-s-triazine] was also observed. However, the identity of this compound could not be confirmed by GC-MS. It should be noted that in our preliminary experiments, it was observed that an aqueous solution of prometryn and dissolved FA or HA kept in the dark did not give the observed photoproducts.

Sensitized photolysis of xenobiotics in agricultural waters was first demonstrated by Ross and Crosby (1973). In an earlier study it was shown that dissolved humic material sensitized the photolysis of atrazine (Khan and Schnitzer, 1978). This work also shows that dissolved FA or HA sensitizes the photolysis of prometryn as indicated by the formation of a mono-N-dealkylated product, namely, 4-amino-6-(isopropylamino)-s-triazine (IV). Zepp et al. (1977) suggested that singlet oxygen formed during photolysis reacts with dissolved organic matter in natural water to form a peroxide. It is possible that the peroxide thus formed may generate the hydroxyl radicals from the humic solution, which in turn causes dealkylation by the removal of the N-alkyl group from the herbicide. This is substantiated by the fact that hydroxyl radicals generated by chemical systems dealkylate s-triazine herbicides (Plimmer et al., 1971).

This study demonstrates the photosensitized formation of 4-amino-6-(isopropylamino)-s-triazine from prometryn in aqueous solutions of FA or HA. The formation of this compound was not observed in the photolysis of prometryn

in distilled water or in an aqueous suspension of HA. The results also demonstrate that the order of the photolytic reaction rate may also be changed by the presence of soluble humic materials. It appears that the photochemical effects of humic materials in the aquatic system will depend on their physical state. In the suspended form, the interior of the humic particles will probably receive no photons so that the production of the photochemically activated species may not be sufficient to cause photosensitization or change in reaction rate. On the other hand, in the presence of dissolved humic materials the concentration of the photochemically activated species available for reaction will be the maximum obtainable for the UV irradiation flux used.

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Singlet Oxygen Generation on Soil Surfaces

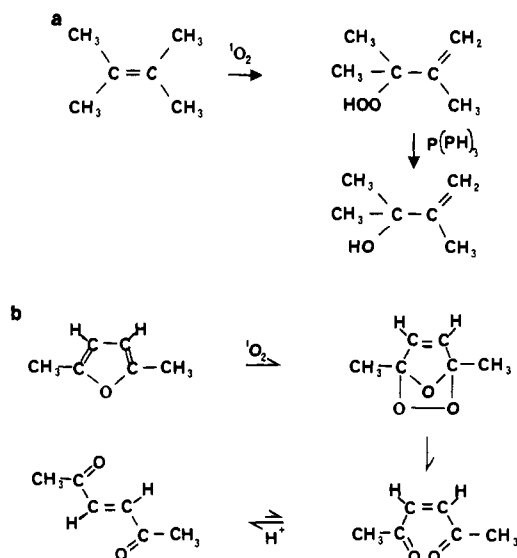
Kirk Gohre and Glenn C. Miller*

Soil is shown to photosensitize two reactions characteristic of singlet oxygen. The soil photooxidation of 2,5-dimethylfuran results in the formation of *cis*- and *trans*-diacetylene. Tetramethylethylene is photooxidized to a hydroperoxyl that is reduced to form 2,3-dimethyl-1-buten-3-ol. The production of both photoproducts suggests that singlet oxygen is formed on soil surfaces and may contribute to indirect photooxidative processes on soil.

Pesticides and other xenobiotics can undergo many different types of degradations when they come into contact with soil surfaces (Stevenson, 1976). Photooxidation reactions can be an important degradation route for these substances, contributing to their detoxification and eventual humidification. For example, parathion is rapidly photooxidized on soil and dust surfaces to the more toxic oxon (Spencer et al., 1980). Oxidation of methidathion on dry soil has also been demonstrated (Smith et al., 1978).

One of the potential mechanisms for photosensitized oxidation on soil surfaces is through production of singlet oxygen. Singlet oxygen production has been demonstrated previously in natural waters (Zepp et al., 1977) by using chemical traps and linked to the presence of naturally occurring humic substances. The mechanism suggested for singlet oxygen formation was through a triplet energy transfer from a photosensitizer, as originally proposed by Kautsky (1937). Additionally, chemiluminescence at 634 nm attributable to a dimole emission of singlet oxygen during the photooxidation of humic acid solutions has been observed (Slawinski et al., 1978). They observed inhibition of the chemiluminescence with both free radical inhibitors

Scheme I



and singlet oxygen quenchers, suggesting sensitized singlet oxygen production by both a radical (type 1) and a triplet-triplet (type 2) sensitization.

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