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

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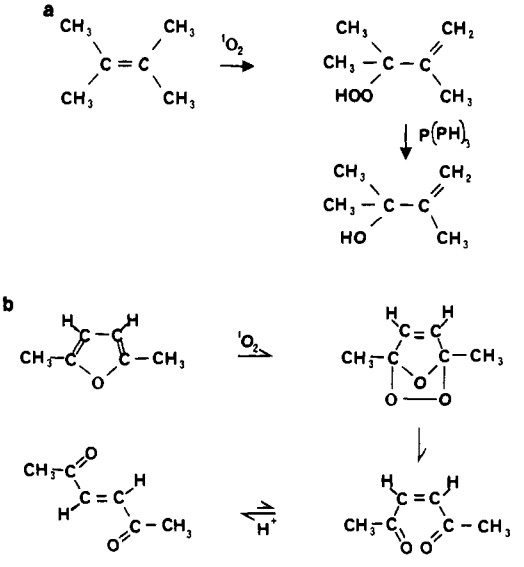
Soil is shown to photosensitize two reactions characteristic of singlet oxygen. The soil photooxidation of 2,5-dimethylfuran results in the formation of *cis*- and *trans*-diacetylethylene. Tetramethylethylene is photooxidized to a hydroperoxyl that is reduced to form 2,3-dimethyl-1-buten-3-ol. The production 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 and singlet oxygen quenchers, suggesting sensitized singlet oxygen production by both a radical (type 1) and a triplet–triplet (type 2) sensitization.

Scheme I



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0021-8561/83/1431-1104$01.50/0

In this study, singlet oxygen was trapped on soil surfaces by using two reactive and well-characterized singlet oxygen traps (Gleason et al., 1970; Foote, 1968). The first trap used was tetramethylethylene (TME), which reacts with singlet oxygen by an "ene" mechanism to form a hydroperoxyl, which is then reduced to the alcohol, 2,3-dimethyl-1-buten-3-ol (DBO) (Scheme Ia). The second trap used was 2,5-dimethylfuran (DMF). Singlet oxygen reacts with DMF by a cycloaddition to form an ozonide that decomposes in water to give *cis*-diacetylethylene (Scheme Ib). *cis*-Diacetylethylene (CDE) can then isomerize to the more stable *trans*-diacetylethylene (TDE).

EXPERIMENTAL SECTION

Reagents. 2,3-Dimethyl-1-buten-3-ol and rose bengal were obtained from ICN-KNK Pharmaceuticals, Inc. Acetonylacetone, benzophenone, 2,5-dimethylfuran, tetramethylethylene, and triphenylphosphine were obtained from Aldrich Chemical Co., Inc. Solvents were Burdick and Jackson distilled in glass spectral grade. *trans*-Diacetylethylene was synthesized from acetonylacetone (Armstrong and Robinson, 1934).

Methods. *Soil Preparation.* A northeastern Montana soil (silty loam, organic matter 3.46%, moisture 3.1%, pH 6.7) was sieved through a screen (0.04 cm) to obtain a uniformly sized sample. Sterilized soil was obtained by autoclaving at 16 psi and 121 °C for 1 and 0.5 h successively.

Tetramethylethylene Assay on Soils. A total of 1.75 g of soil was added to a 50-mL volumetric flask. This gave a soil depth of approximately 1–2 mm and a surface area in the flask of 14.5 cm^2. The flask was evacuated and refilled with nitrogen, oxygen, or air and stoppered with a silicone septum. TME (5 μL, 4.2×10^{-5} mol) was then injected into the flask and the liquid immediately evaporated. No attempt was made to further mix the chemical into the soil. Irradiation was accomplished by direct sunlight or by an apparatus containing four CW40 Westinghouse fluorescent lights. The photoproduct, 2,3-dimethyl-3-hydroperoxy-1-butene, was reduced to DBO by the addition of 6 mL of 0.05 M triphenylphosphine in methanol. The flasks were covered to prevent further light exposure and refrigerated, and the reduction of the hydroperoxide was allowed to proceed for 1 h prior to analysis. The cooled solution was centrifuged on a desk top centrifuge and the supernatant immediately analyzed by flame ionization gas chromatography. The column was a 1.2 m × 2 mm i.d. nickel column containing 100–120-mesh Poropak S. The column temperature was 195 °C. Under these conditions, TME and DBO had retention times of 1.9 and 5.1 min, respectively. Both chemicals were quantitated by comparing peak heights with those of known standards.

DMF Assay on Soils. A 50-mL volumetric flask, soil, and designated atmosphere were prepared as described for TME. DMF (5 μL, 4.6×10^{-5} mol) was injected into the flask and irradiated as before. The reaction was stopped with the addition of 6 mL of methanol and the flask covered. A portion of the yellow methanol soil extract was drawn from the flask within 30 min after irradiation and filtered through a 0.45-μm Gelman filter. The resulting yellow filtrate was analyzed by HPLC. Operating conditions were as follows: Altex 5-μm ultrasphere ODS column, 15 cm × 4.6 mm i.d.; detector, Perkin-Elmer, UV variable wavelength, at 225 nm; mobile phase, 15% methanol/water at 1 mL/min. The products, *cis*- and *trans*-diacetylethylene, were quantitated by comparison of the peak height with that of a known standard. The cis and trans isomers had retention times of 4 and 5.1 min, respectively.

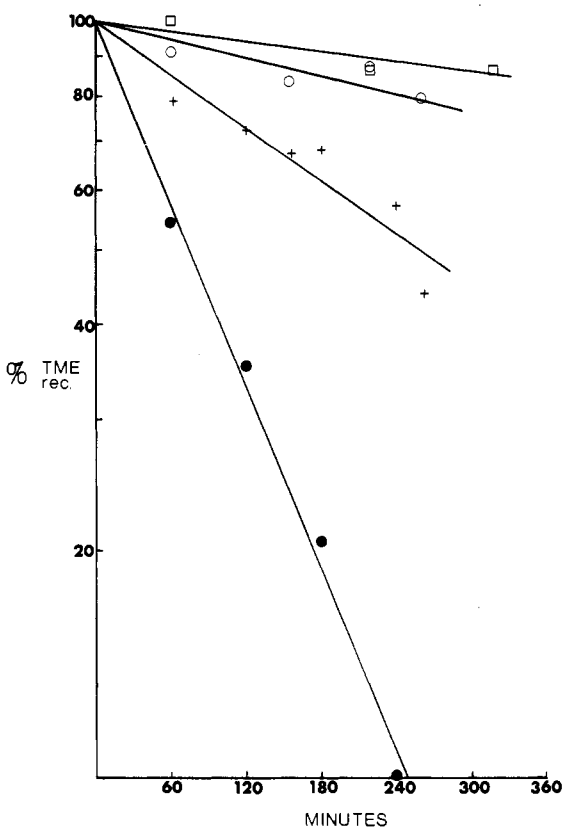

Figure 1. Sunlight irradiation of TME on soil, Aug 29, 1981. (□) A bare flask irradiated under an oxygen atmosphere; (○) soil under an oxygen atmosphere nonirradiated; (+) soil irradiated under a nitrogen atmosphere; (●) soil irradiated under an oxygen atmosphere.

DMF in the remaining methanol–soil slurry was quantitated following centrifugation by gas chromatography at 190 °C on the previously described column.

Identification of Photoproducts. DBO was identified by comparison of gas chromatographic retention times and mass spectra (Finnagan 4023 gas chromatograph–mass spectrometer) with those of a known standard. TDE was identified by comparing the liquid chromatographic retention time with that of a synthesized standard and also by irradiating 1 g of dimethylfuran on 50 g of soil, collecting the product, and determining the melting point of its bis(2,4-dinitrophenyl)hydrazone [276–278 °C; lit. 277 °C (Levisalles, 1957)]. CDE was identified by comparing its liquid chromatographic retention time to that of CDE made by photoisomerizing TDE in benzene with benzophenone (Zepp et al., 1977). First-order rate constants were determined by using a least-squares analysis.

RESULTS

TME Irradiation. The sunlight photooxidation of TME on the Montana soil (Figure 1) could be approximated as a first-order reaction. Sunlight irradiation in either an oxygen or air atmosphere was required for production of the singlet oxygen product, DBO, as expected for a photosensitized oxidation. Although loss of TME from a bare flask containing oxygen atmosphere was observed, the rate of TME loss was substantially slower and none of the singlet oxygen product was formed. Irradiation of the Montana soil under a nitrogen atmosphere also resulted in an intermediate rate of TME degradation and no alcohol product was observed. Samples kept with soil under an oxygen atmosphere in the dark also resulted in slow TME loss and no alcohol product. When the nonirradiated samples were subjected to a temperature of 50

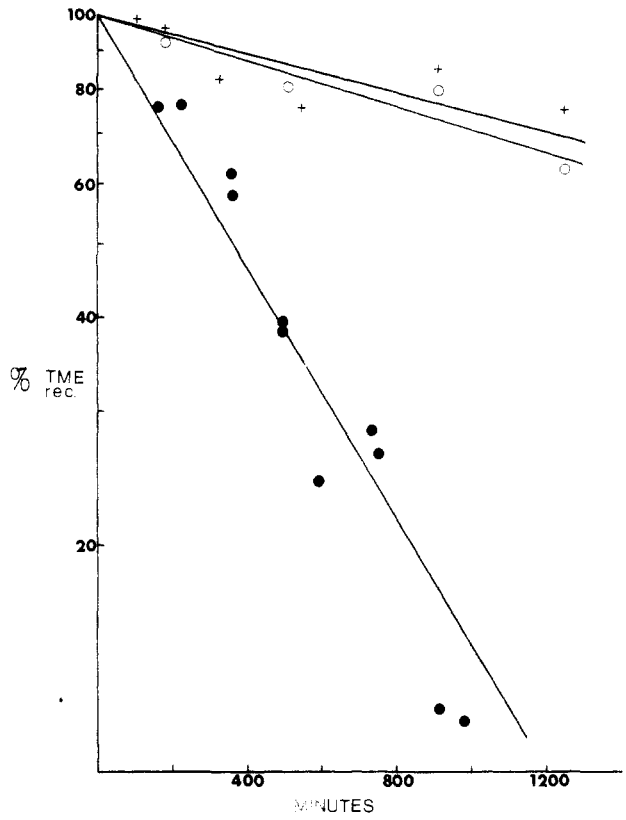

Figure 2. CW40 irradiation of TME on soil. (○) Soil under an oxygen atmosphere nonirradiated; (+) soil irradiated under a nitrogen atmosphere; (●) soil irradiated under an oxygen atmosphere.

Table I. Rates of Photolysis of TME

light source	conditions	k_p, min^{-1},[a] × 10^3	r^2
sunlight	O_2, bare flask	0.56	0.89
dark[b]	O_2, soil	0.58	0.74
sunlight	N_2, soil	2.6	0.90
sunlight	O_2, soil	9.2	0.99
CW40	N_2, soil	0.23	0.66
dark[b]	O_2, soil	0.34	0.92
CW40	O_2, soil	2.3	0.95

[a] k_p is the first-order rate constant for photolysis of TME. [b] Aluminum foil covered flask set in the sunlight or under the CW40 lamps.

°C over 8 h, 75% of the TME was recovered with no trace of the alcohol product. Thus, the oxidation products were not thermally generated.

The photooxidation of TME with Westinghouse CW40 fluorescent lamps was also examined. Use of CW40 Westinghouse lights afforded a method that gave consistent and comparable data from day to day. The CW40 lamps (which have low ultraviolet intensities) gave similar results to sunlight irradiation but higher yields of the alcohol product (Figure 2). The rate of loss of TME under nitrogen atmosphere on soil was similar to that of the nonirradiated sample, which suggests that the low ultraviolet, visible CW40 light is less able to promote the non-oxygen-dependent degradations observed when TME was exposed to sunlight in a nitrogen atmosphere.

First-order rate constants for loss of TME were calculated in each case and presented in Table I. As can be seen, the correlation coefficients are low for the systems that lacked soil or were not irradiated, and constraining these data to first-order kinetics is questionable. However,

Table II. Irradiations of TME on Soil Using Sunlight and CW40 Lamps[a]

light source	atmosphere	% TME recovered	% conversion to alcohol
sunlight[b]	O_2	n.d.[c]	18.0
sunlight[b]	air	12.3	7.7
sunlight[b]	N_2	38.2	n.d.
CW40 lamps[d]	O_2	n.d.	26.8
CW40 lamps[d]	air	15.6	14.7
CW40 lamps[d]	N_2	52.0	n.d.
sunlight[e]	O_2	29	8.0
sunlight[f]	O_2	44	9.8

[a] All data represent the average of three trials. [b] Exposed outdoors for 48 h Nov 20, 1980. [c] Not detected. [d] 24-h irradiation. [e] 4 h of noonday sun Aug 14, 1982. [f] 4 h of noonday sun Sept 4, 1982.

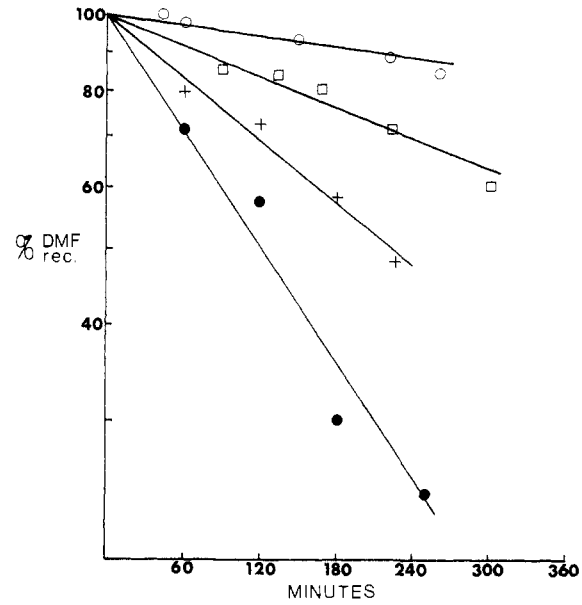

Figure 3. Sunlight irradiation of DMF on soil, Aug 28, 1981. (○) Soil under an oxygen atmosphere nonirradiated; (□) a bare flask irradiated under an oxygen atmosphere; (+) soil irradiated under a nitrogen atmosphere; (●) soil irradiated under an oxygen atmosphere.

the relative rates provide a basis for comparison. In both sunlight and the artificial lamps, the rate constants for photolysis in the presence of oxygen were at least 3 times greater than that of the other systems.

The conversion of TME to DBO when irradiated with sunlight or CW40 lamps is presented in Table II. DBO production accounts for up to 27% of the TME loss under these conditions. This is the minimum conversion percentage since loss of DBO would result in an underestimation of the conversion yield. When DBO was irradiated by using CW40 lamps for 27 h on soil in a separate experiment, 7% was lost. In August sunlight, however, during a 4-h exposure, 48% of the starting DBO was lost. The higher loss in sunlight may be due to both photochemical and also thermal effects, since the temperature of the surface on which the flasks were placed was at times observed up to 60 °C.

DMF Irradiation. The sunlight irradiations of DMF on the same Montana soil gave results similar to the TME photooxidations (Figure 3). As before, DMF loss could be approximated as a first-order reaction, and as expected, oxygen and sunlight were required for the production of the singlet oxygen products, *cis*- and *trans*-diacetylethylene. Lower loss of DMF was observed when irradiated in a bare flask under oxygen atmosphere with no

Table III. Rates of Photolysis of DMF

light source	conditions	k_p, min^{-1},[a] $\times 10^3$	r^2
dark[b]	O_2, soil	0.57	0.97
sunlight	O_2, bare flask	1.6	0.97
sunlight	N_2, soil	3.1	0.97
sunlight	O_2, soil	5.6	0.94
dark[b]	O_2, soil	0.35	0.72
CW40	N_2, soil	0.41	0.88
CW40	O_2, soil	1.8	0.98

[a] k_p is the first-order rate constant for photolysis of DMF. [b] Aluminum foil covered flask set in the sunlight or under the CW40 lamps.

Table IV. Irradiation of DMF on Soil Using Sunlight and CW40 Lamps

light source	time of exposure, h	atmosphere	% DMF recovered	% conversion to *trans*-diacetylethylene
sunlight[a]	4.2	O_2	21	5.8
sunlight	4.2	N_2	65	n.d.[b]
CW40 lamps	9.5	O_2	42	10.0
CW40 lamps	7.5	O_2	52	6.4
CW40 lamps	7.0	N_2	83	n.d.

[a] Exposed during midday (Aug 11, 1981). [b] Not detected.

production of the singlet oxygen product. Irradiation of DMF on soil under a nitrogen atmosphere resulted in greater DMF loss and no production of diacetylethylene. Samples containing soil under an oxygen atmosphere held in the dark indicated slow DMF loss with no production of the diacetylethylene. As in the TME experiments, heating DMF to 50 °C in oxygenated flasks containing soil also gave no singlet oxygen products.

Photooxidations of DMF on soil were also done with CW40 lights. Oxygen and light were again essential for the production of diacetylethylene. Dark controls and samples irradiated either in a nitrogen atmosphere or in the absence of soil showed less DMF loss and no singlet oxygen products (Figure 4).

First-order rate constants for loss of DMF are presented in Table III. In both sunlight and under artificial lamps the rate of DMF loss in the presence of oxygen was substantially greater than under any other conditions. Table IV indicates results of TDE formation in sunlight and CW40 lights under various conditions.

The HPLC chromatograms (Figure 5) obtained for photooxidation of DMF on soil surfaces and in water containing rose bengal, a well-known singlet oxygen sensitizer, show two distinct peaks that were identified as *cis*- and *trans*-diacetylethylene. Both the cis and trans peaks observed on soil photooxidations of DMF cochromatographed with the photooxidation products of DMF with rose bengal in water. The peak corresponding to CDE was the major peak observed in rose bengal–DMF photooxidation and the minor peak in soil photooxidations of DMF. When both solutions were allowed to sit at room temperature for several days, TDE was the major fraction in both samples due to isomerization to the more stable trans product. It appears also reasonable that on the soil surface the ozonide initially breaks down to the cis isomer, which then isomerizes to the more stable trans isomer. Preferential formation of the trans isomer has been observed previously (Gleason et al., 1970). The isomerization of CDE to TDE has also been observed in surface water

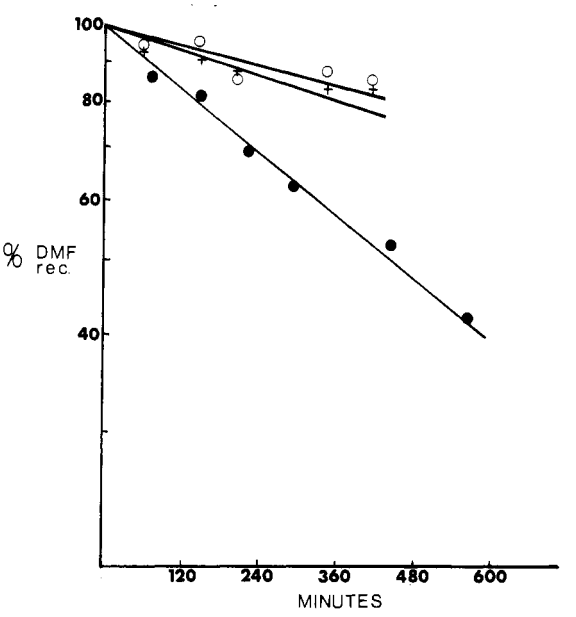

Figure 4. CW40 irradiation of DMF on soil. (○) Soil under an oxygen atmosphere nonirradiated; (+) soil irradiated under a nitrogen atmosphere; (●) soil irradiated under an oxygen atmosphere.

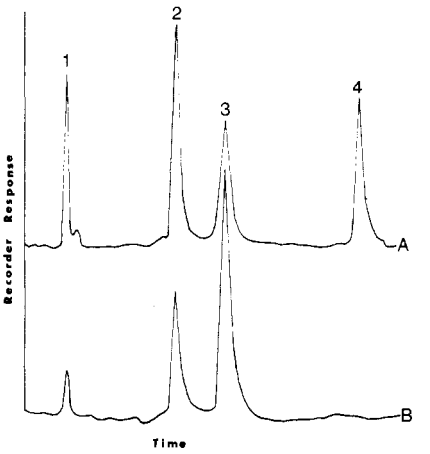

Figure 5. HPLC chromatograms of the photooxidation products of DMF: (A) with rose bengal sensitizer in water and (B) on soil. Peak 1, rose bengal; peak 2, *cis*-diacetylethylene; peak 3, *trans*-diacetylethylene; peak 4, ozonide of DMF.

(Wolff et al., 1981). The peak observed at 8.8 min during rose bengal–DMF photooxidations was identified as the ozonide of DMF by its conversion to diacetylethylene upon addition of triphenylphosphine. This ozonide was not observed on soil DMF photooxidations, presumably due to rapid reduction on the soil surface. In addition, triphenylphosphine was not found to be essential for reduction of 2,3-dimethyl-3-hydroperoxy-1-butene to the alcohol, although use of the reducing agent resulted in optimal yields.

Sterilized soil was tested to see if its photooxidation properties were different than those of unsterilized soil. Table V shows that no significant differences in the singlet oxygen products for TME or DMF were observed, indicating that the oxidations were not due to microbial processes.

DISCUSSION

The photooxidation of DMF and TME to the characteristic singlet oxygen products strongly suggests that singlet oxygen is being generated on soil surfaces by a photosensitized reaction. This component of soil acting as the sensitizer is assumed to be the organic fraction of

Table V. Photooxidation of TME and DMF on Sterilized Montana Soil[a]

substrate added	% DMF recovered	% TDE recovered	% TME recovered	% DBO recovered
sterilized soil, 5 μL of TME			37.5	9.3
unsterilized soil, 5 μL of TME			36.0	11.0
sterilized soil, 5 μL of DMF	47.0	8.5		
unsterilized soil, 5 μL of DMF	49.0	7.8		

[a] All points represent duplicate trials of CW40 photooxidations for 7.75 h.

the soil, although inorganic compounds, such as oxides of titanium and zinc, have also been implicated as singlet oxygen sensitizers (Pappas and Fischer, 1974; Wasserman and Murray, 1979). Thermal and biological processes appear not to be involved.

Products characteristic of the singlet oxygen reaction for TME and DMF can, however, also be produced by other reaction mechanisms. Foote has suggested that dicarbonyl compounds can be made from furans by other reactions (Foote, 1978). DBO can be produced from TME with rhodium and iridium complexes in the presence of oxygen at 50 °C (Lyons and Turner, 1972). The authors suggested a radical-initiated oxidation due to the observation that the reactions were inhibited by hydroquinone. Since our attempts at thermal oxidations at 50 °C under oxygen atmosphere failed, a radical mechanism is probably not involved. DBO has also been made from TME by gas-phase oxidations but at elevated temperatures (Ray and Waddington, 1973). On soils, radical reactions forming DBO are also possible since humic acid and fulvic substances contain stable free radicals that, upon irradiation, show increased concentrations of transient free radicals (Choudhry, 1981). Soil that was preexposed to sunlight followed by TME or DMF addition and allowed to sit in the dark showed minor substrate loss and no production of the singlet oxygen like products. This fact, coupled with the failure to thermally generate the products, suggests that radical oxidants, while likely to be present, are not responsible for the reactions observed. The slower loss of both compounds when irradiated in a nitrogen atmosphere does, however, indicate other degradative pathways.

In midday sunlight and an oxygen atmosphere, both TME and DMF exhibited surprisingly short photolysis half-lives, 85 and 120 min, respectively. While reaction with singlet oxygen is probably the predominant pathway for loss of these substrates, other strong oxidants, such as peroxyl, hydroxyl, superoxide, and other radicals, are also potentially being generated on soil surfaces during irradiation. The production of singlet oxygen and these other oxidants on soil surfaces during sunlight irradiation could be important in the transformation and permanent binding of pesticides and other organic molecules to soil components.

Registry No. DMF, 625-86-5; TME, 563-79-1; TDE, 820-69-9; CDE, 17559-81-8; DBO, 10473-13-9; O_2, 7782-44-7.

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