

Photochemistry of Metalaxyl

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The photolysis of the fungicide metalaxyl in aqueous solution has been examined. Irradiation at 254 and 290 nm resulted, respectively, in 53 and 10% substrate transformation in 3 h. Long-time (65 h) irradiation under artificial sunlight in the presence of commercially available humic acid resulted in 65% degradation of the chemical. The photolysis leads not only to rearrangement of the *N*-acyl group to the aromatic ring but also to demethoxylation, *N*-deacylation, and elimination of the methoxycarbonyl group from the molecule.

Metalaxyl [*N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-alanine methyl ester, I; Figure 1] is a systemic fungicide widely used to control plant diseases caused by oomycetes fungi of the order Peronosporales (Schwinn et al., 1977; Houseworth, 1987). The mobility, metabolism in soil, and microbial degradation are well documented (Cohen and Coffey, 1986; Sharom and Edington, 1982), and the compound has been found to persist for nearly 4 weeks in Pearl millet and lettuce (Singh et al., 1986; Cho, 1981). Earlier studies (Burkhard, 1979; Yao et al., 1989) of the photolysis of metalaxyl have described the formation of metalaxyl acid and *N*-(2,6-dimethyl-4-acetylphenyl)alanine methyl ester. The rate of photodegradation and the chemical nature of the photoproducts of metalaxyl irradiated with UV light ($\lambda = 254$ and 290 nm) are reported here. In addition, the effect of commercially available humic acid (potassium salt) on the rate of degradation of metalaxyl in artificial sunlight is also discussed.

EXPERIMENTAL PROCEDURES

Materials. Metalaxyl, analytical standard grade (99%), was supplied by Riedel-de Haën, Germany, and was purified further by repeated recrystallization from a mixture of hexane and methanol to a mp of 75 °C. 2,6-Dimethylacetanilide (97%) was purchased from Aldrich Chemical Co. and was used without purification for comparison. Methyl 2-bromopropionate (99%), 2,6-dimethylaniline (99%), ethyl iodide, acetyl chloride (99%), and methoxyacetyl chloride (99%) were also obtained from Aldrich and were used to synthesize comparison products. Humic acid potassium salt was obtained from Carl-Roth KG. All solvents used were of AR grade.

Apparatus. Quantitative HPLC analysis of metalaxyl was carried out with a Gilson-Abimed Model 302 liquid chromatograph equipped with a Shandon reversed-phase column (RP-18, 25 × 0.4 cm i.d.) and a UV detector set at 218 nm; the mobile phase was methanol-water (60:40, adjusted to pH 4.0 with 0.15 M H₃PO₄, flushed with helium, flow rate, 0.5 mL/min). A Gilson-Abimed Model 305 HPLC, equipped with a Microsorb C₁₈ reversed-phase column (Rainin Instruments Co., 25 cm × 1.0 cm i.d.), and a UV detector set at 218 nm were used to separate the photoproducts on a preparative scale. The mobile phase was the same as for the quantitative analysis (flow rate, 1 mL/min). A Hewlett-Packard Model 59928 GC-MS instrument at an ionization potential of 70 eV was used to obtain the mass spectra. The GC conditions were as follows: a Macherey-Nagel capillary column (PermaBond SE-52; 25 m × 0.35 mm i.d.) coated with a 0.5- μ m film of phenyl ethyl silicone; injector temperature, 230 °C; carrier gas, helium; temperature program, 70–250 °C, 10 °C/min. The sample was injected in splitless mode. ¹H and ¹³C

NMR spectra (400 and 100 MHz, respectively) of CDCl₃ solutions were obtained on a Bruker 400 AC instrument with TMS as an internal standard.

Irradiation. I (10 mg, 50 ppm) in 200 mL of deionized water was irradiated for 180 min with a high-pressure mercury lamp (HPK 125 W, Philips) jacketed with a water-cooled quartz filter to get maximum intensity of UV light down to $\lambda = 250$ nm. Similar experiments with I were performed in deionized water with a Pyrex filter ($\lambda \geq 290$ nm). To investigate the effect of humic acid on the photodecomposition of metalaxyl, 10 mg of humic acid (potassium salt) was added to an aqueous solution (50 mg/L) of the pesticide, and the solution was irradiated in a Suntest apparatus (Heraeus, Hanau, Germany). According to the manufacturer's specifications, the lamp emits light with a spectrum close to that of sunlight (300–800 nm). Samples of I in aqueous solutions with and without humic acid were held in the dark as controls.

Preparation of Comparison Compounds. *N*-(Methoxyacetyl)-2,6-dimethylaniline (Photoproduct IV, Figure 1). Methoxyacetyl chloride (1.1 g, 0.2 mol) was added to a solution of 2,6-dimethylaniline (1 g, 0.165 mol) in dry toluene (50 mL), and the mixture was heated at reflux for 3.5 h, cooled to ambient temperature, and washed successively with 10% aqueous Na₂CO₃ (three times, 20 mL each) and water (three times, 20 mL each); the organic phase was dried over Na₂SO₄. After removal of the solvent at reduced pressure, the resulting light green oil was purified by column chromatography on silica gel 60 with ethyl acetate-hexane (30:70): ¹H NMR δ 2.18 (s, 6 H), 3.4 (s, 3 H), 3.9 (s, 2 H), 7.8 (br s, 1 H); ¹³C NMR δ 167.9 (carbonyl), 135.3, 133.0, 128.1, 127.3 (aromatic carbons), 72.0 (OCH₂), 59.3 (OCH₃), 18.3 (arylmethyls).

N-Ethyl-2,6-dimethylaniline. A mixture of 2,6-dimethylaniline (2 g, 0.33 mol), K₂CO₃ (1 g), ethyl iodide (2.6 g, 0.33 mol), and acetone (50 mL) was stirred at room temperature for 8 h. The mixture was then filtered, and the insoluble inorganic salts were washed with acetone. The filtrate and the washings were combined, and the solvent was removed at reduced pressure. The residue, a liquid, was taken into ethyl acetate and washed successively with 10% HCl and H₂O. The organic phase, after being dried over Na₂SO₄, was concentrated on a rotary evaporator to afford a light yellow liquid that was subjected to column chromatography (silica gel 60). The fraction eluted with 2% ethyl acetate in *n*-hexane gave, after removal of the solvent, *N*-ethyl-2,6-dimethylaniline: MS M⁺ 149, fragments at 134 (M - CH₃), 120 (M - C₂H₅), 105 (M - C₂H₅, -CH₃).

2,6-Dimethyl-*N*-ethylacetanilide (Photoproduct VIII, Figure 1). A mixture of *N*-ethyl-2,6-dimethylaniline (1 g, 0.165 mol), acetyl chloride (0.53 g, 0.014 mol), and dry toluene (50 mL) was heated at reflux for 3 h, cooled to room temperature, washed with Na₂CO₃ (10%) and water, and then dried (Na₂SO₄). Evaporation of the solvent gave a liquid, which after purification on a silica gel column (Merck 60, 20% ethyl acetate in *n*-hexane), afforded VIII: ¹H NMR δ 1.13 (t, *J* = 7.3 Hz, 3 H), 1.71 (s, 3 H), 2.23 (s, 6 H), 3.67 (q, *J* = 7.3 Hz, 2 H), 7.1–7.2 (m, 3 H); ¹³C δ 170.6 (carbonyl), 140.5, 136.0, 128.9, 127.9 (aromatic carbons), 43.0, and 13.0 (*N*-ethyl group).

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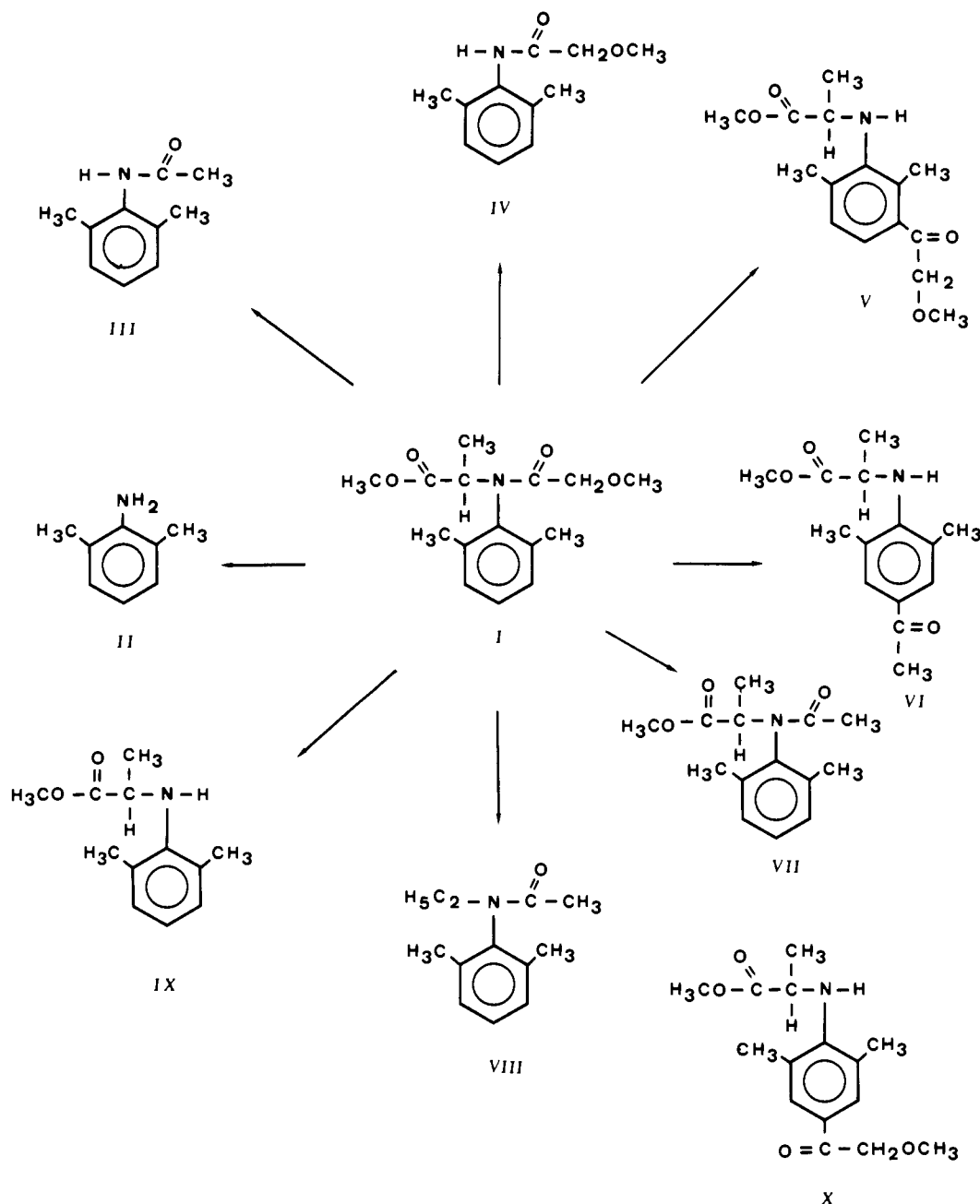


Figure 1. Photoproducts identified following irradiation of metalaxyl in aqueous medium.

N-(2,6-Dimethylphenyl)alanine Methyl Ester (Photoproduct IX, Figure 1). To a stirred mixture of 10 g (1.65 mol) of 2,6-dimethylaniline and K_2CO_3 (10.7 g) in 50 mL of acetone was added 13.8 g (1.65 mol) of methyl 2-bromopropionate. The reaction mixture was stirred for 16 h at room temperature. The usual workup, followed by chromatography (silica gel 60, elution with 3% ethyl acetate in *n*-hexane), afforded IX as a liquid: 1H NMR δ 1.37 (d, J = 6.9 Hz, 3 H), 2.29 (s, 6 H), 3.64 (s, 3 H), 3.97 (q, J = 6.1 Hz, 1 H), 3.76 (br s, 1 H), 6.79 (t, J = 7.4 Hz, 1 H), 6.95 (d, J = 7.5 Hz, 2 H); ^{13}C δ 143.9, 128.93, 128.9, 121.8 (aromatic carbons), 175.9 (carbonyl), 51.9 (OCH₃), 55.0 (NCH), 19.7 (alanine methyl), and 18.7 (arylmethyl carbons).

N-(2,6-Dimethylphenyl)-*N*-acetylalanine Methyl Ester (Photoproduct VII, Figure 1). Compound IX (1 g) and acetyl chloride (0.38 g) were heated at reflux for 3 h in dry toluene. Workup of the reaction mixture as in the case of compound VIII yielded VII: 1H NMR δ 1.01 (d, J = 7.4 Hz, 3 H), 1.73 (s, 3 H), 2.15 (s, 3 H), 2.47 (s, 3 H), 3.79 (s, 3 H), 4.50 (q, J = 7.1 Hz, 1 H), 7.12 (dm, J = 7.1 Hz, 1 H), 7.12 (dm, J = 7.1 Hz, 1 H), 7.17 (dm, J = 8.0 Hz, 2 H); ^{13}C δ 173.2 and 171.4 (amide and ester carbonyl), 138.5, 137.8, 137.2, 129.2, 128.6, 128.5 (aromatic carbons), 55.1 (NCH), 52.1 (OCH₃), 21.9 (acetyl CH₃), 18.2 and 18.5 (arylmethyl carbons), 15.2 (alanine CH₃).

Isolation and Identification of Photoproducts. To produce enough of the photoproducts for structural analysis, a solution of 500 mg of I in 1 L of deionized water was irradiated in five batches (100 mg in 200 mL) for 3 h through a quartz filter. The irradiated solutions were combined and extracted with diethyl ether (three times, 200 mL each). The organic phase after drying (anhydrous Na_2SO_4) and concentration at reduced pressure afforded a brown liquid. A solution of this liquid in methanol (2 mL) showed on GC analysis, in addition to metalaxyl, a number of products. Separation of the unchanged metalaxyl and its photoproducts was achieved by semipreparative HPLC (100 μ L per injection) with methanol-water (60:40, adjusted to pH 4.0 with 0.15 M H_3PO_4) as eluent. Nine main fractions (1–9 in order of increasing retention times) were collected. Corresponding eluates from several injections were combined, and the solvent was removed on a rotary evaporator.

Fraction 1 (R_t 6.58 min). The amount of this fraction was so small that, except for mass analysis, no spectral data could be obtained. The mass spectrum (molecular ion m/z 121 and fragments recorded in Table I) was comparable with the mass spectrum of 2,6-dimethylaniline (II, Figure 1). Furthermore, the GC retention time of this fraction (14.29 min) was the same as that of the standard.

Table I. Preparative HPLC—Retention Time and Mass Spectral Data of Photodecomposition Products of I

product	retention time, min	mass found	% abundance	structure
II	6.58	121	100.0	M ⁺
		106	27.3	M ⁺ - CH ₃
		91	24.2	M ⁺ - HCNH - CH ₃
		77	34.6	C ₆ H ₅ ⁺
III	12.02	163	56.6	M ⁺
		121	100.0	M ⁺ - COCH ₃ + 1
		106	57.5	M ⁺ - COCH ₃ - CH ₃ + 1
		91	17.4	M ⁺ - COCH ₃ - 2CH ₃ + 1
IV	14.06	77	25.6	C ₆ H ₅ ⁺
		193	56.6	M ⁺
		163	16.2	M ⁺ - OCH ₃ + 1
		148	100.0	M ⁺ - CH ₂ OCH ₃
		134	46.8	M ⁺ - OCH ₃ - 2CH ₃ - 1
		120	62.7	M ⁺ - COCH ₂ OCH ₃ - 1
		105	47.9	M ⁺ - COCH ₂ OCH ₃ - CH ₃ - 1
V	25.94	91	29.6	C ₆ H ₅ CH ₂ ⁺
		279	26.4	M ⁺
		234	100.0	M ⁺ - CH ₂ OCH ₃
		220	53.0	M ⁺ - CH ₂ OCH ₃ - CH ₃ + 1
		146	25.8	M ⁺ - COCH ₂ OCH ₃ - OCH ₃ - 2CH ₃ + 1
VI	34.85	77	12.2	C ₆ H ₅ ⁺
		249	22.9	M ⁺
		190	100.0	M ⁺ - COOCH ₃
		148	33.5	M ⁺ - COOCH ₃ - COCH ₃ + 1
VII	36.77	77	12.2	C ₆ H ₅ ⁺
		249	14.5	M ⁺
		190	26.1	M ⁺ - COOCH ₃
		148	100.0	M ⁺ - COOCH ₃ - COCH ₃ + 1
VIII	40.10	77	12.2	C ₆ H ₅ ⁺
		191	38.6	M ⁺
		176	12.9	M ⁺ - CH ₃
		148	39.0	M ⁺ - COCH ₃
		134	42.0	M ⁺ - COCH ₃ - CH ₃ + 1
		120	15.2	M ⁺ - COCH ₃ - C ₂ H ₅ - 1
XI	66.12	91	23.8	C ₆ H ₅ CH ₂ ⁺
		77	25.7	C ₆ H ₅ ⁺
		207	17.2	M ⁺
		148	100.0	M ⁺ - COOCH ₃
		105	97.0	M ⁺ - COOCH ₃ - HCNH - CH ₃
		77	11.9	C ₆ H ₅ ⁺

Fraction 2 [Colorless Solid (*R_t*, 12.02 min); Molecular Ion *m/z* 163 (Fragments Reported in Table I)]. The mass spectra and GC (*R_t*, 22.9 min) were in good agreement with those of the standard 2,6-dimethylacetanilide (III, Figure 1). Other spectral data could not be obtained, because the amount of this fraction was also too small.

Fraction 3 [Light Green Liquid (*R_t*, 14.06 min); *m/z* 193 (Fragments Reported in Table I); GC *R_t*, 23.54 min]. This was identified as *N*-(methoxyacetyl)-2,6-dimethylaniline (IV, Figure 1) by direct chromatographic (GC and HPLC) and spectroscopic comparison with an authentic sample of this compound synthesized as described above.

Fraction 4 [Colorless Liquid (*R_t*, 25.94); Molecular Ion *m/z* 279 (Fragments, See Table I)]: ¹H NMR δ 1.38 (d, *J* = 7.0 Hz, 3 H), 2.37 (s, 3 H), 2.35 (s, 3 H), 3.47 (s, 3 H), 3.67 (s, 3 H), 4.12 (q, *J* = 7.0 Hz), 7.03 (br d, *J* = 7.9 Hz, 1 H), and 7.05 (d, *J* = 7.8 Hz, 1 H) (V, Figure 1).

Fraction 5 [Solid (*R_t*, 30.9 min); mp 72 °C]. MS and NMR data were in good agreement with those of metalaxyl (I, Figure 1).

Fraction 6 [Liquid (*R_t*, 34.85); *m/z* 249 (Fragments Reported in Table I)]. Its ¹H NMR and mass spectra were comparable with those of [*N*-(2,6-dimethyl-*p*-acetylphenyl)]alanine methyl ester (VI, Figure 1; Yao et al., 1989).

Fraction 7 [Light Brown Liquid (*R_t*, 36.77; *m/z* 249 (Fragments Listed in Table I) (GC *R_t*, 29.57 min)]. This was identified as

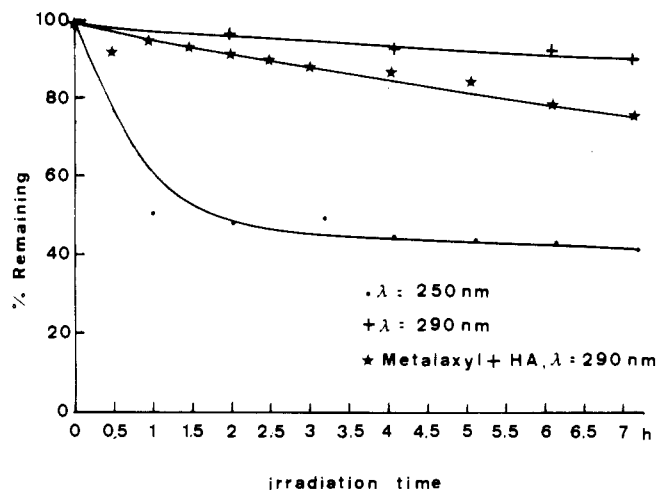


Figure 2. Photodegradation of metalaxyl (10 ppm solution in deionized water) at two different wavelengths and in the presence of humic acid ($\lambda = 290$ nm).

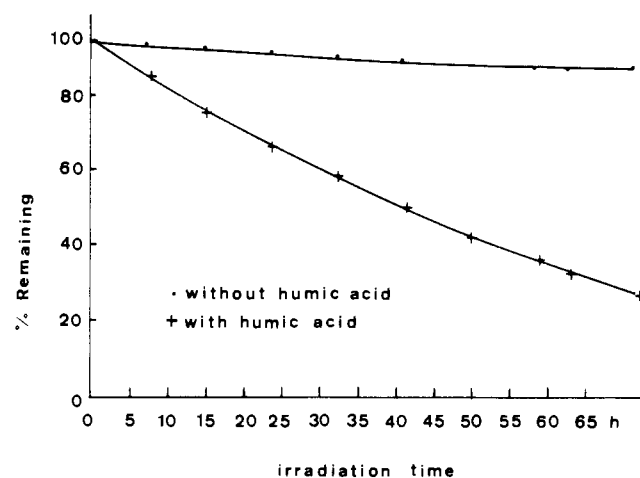


Figure 3. Photodegradation of metalaxyl in the presence of humic acid in artificial sunlight (Suntest experiment).

[*N*-(2,6-dimethylphenyl)-*N*-acetyl]alanine methyl ester by direct comparison of its mass, ¹H NMR, and ¹³C NMR spectra and chromatographic behavior with those of the synthesized compound (VII, Figure 1).

Fraction 8 [Colorless Liquid (*R_t*, 40.1 min; Molecular Ion *m/z* 191 (Fragments Reported in Table I)]. This was identified as 2,6-dimethyl-*N*-ethylacetanilide (VIII, Figure 1) by direct chromatographic (GC, *R_t*, 23.28 min) and spectroscopic comparison with the authentic standard.

Fraction 9 [Light Brown Liquid (*R_t*, 66.12 min); *m/z* 207 (Fragments in Table I)]. MS, ¹H NMR, and ¹³C spectra were in good agreement with those of *N*-(2,6-dimethylphenyl)alanine methyl ester (IX, Figure 1).

RESULTS AND DISCUSSION

A solution of metalaxyl (10 ppm; I, Figure 1) in deionized water was irradiated with UV light at $\lambda = 250$ nm. The results of three such runs showed that after 3 h of irradiation $50 \pm 3\%$ of I was consumed, whereas the compound decomposed only slowly (less than 10% in 3 h) when irradiated at 290 nm. Prolonged irradiation (7 h) under identical conditions led to no further decrease in the substrate concentration, as shown in Figure 2. Irradiation of I ($\lambda = 290$ nm) in the presence of humic acid (10 ppm) led to faster degradation (22%, 7 h) than in its absence (10%, Figure 2). Prolonged irradiation (Suntest equipment) of an aqueous solution of I (10 ppm) showed a marked dependence of the conversion on the presence of humic acid in the solution (nearly 60% conversion in

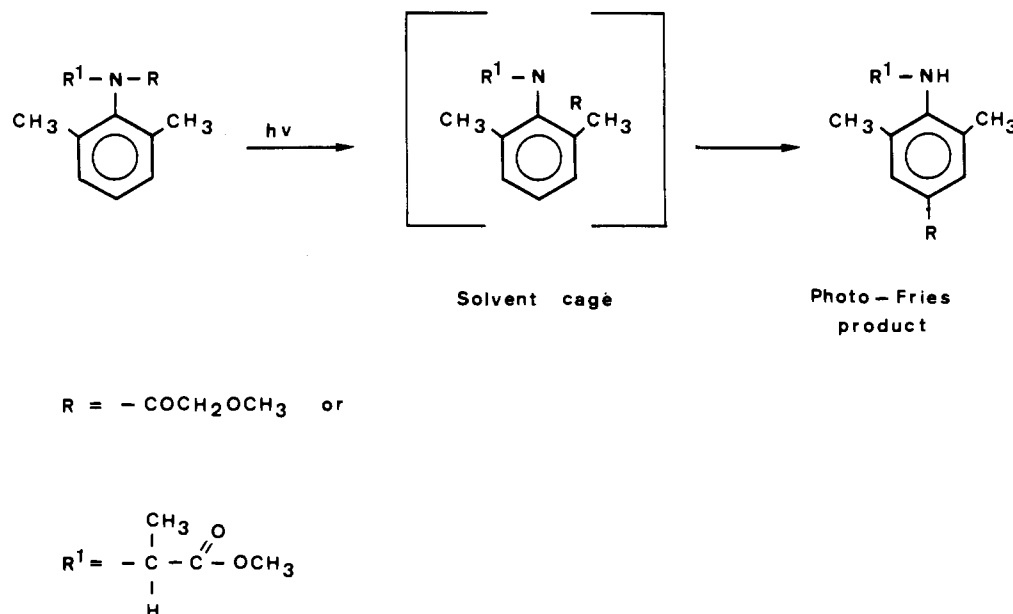


Figure 4. Proposed reaction mechanism of the photo-Fries product [in analogy to the mechanism of Schwetlick et al. (1972)].

65 h, Figure 3). In control experiments (not irradiated) with and without humic acid, there was no degradation of I. Humic acid probably produces active oxygen species that degrade I. Humic acid is an important ingredient of soil, and soil has been reported to produce active oxygen species (Gohre and Miller, 1983; Smith et al., 1978; Slowinski et al., 1978). Compounds IV and IX (Figure 1) were the main photoproducts identified after I was irradiated ($\lambda = 290$ nm and in Suntest) in the presence of humic acid. HPLC analysis of an irradiated aqueous solution of I ($\lambda = 250$ nm) revealed many products. Semipreparative HPLC separation on a RP-18 reversed-phase column afforded eight compounds in addition to metalaxyl (Figure 1). Compounds IV, VIII, and IX are the major photoproducts, followed by V–VII; products II and III are minor ones. The photodecomposition of metalaxyl involves mainly N-dealkylation and demethoxylation in addition to processes like rearrangement of the N-acyl group to the 4-position of the aromatic ring and elimination of the methoxycarbonyl group and alanine methyl ester. The formation of compounds II, VI, and IX is probably the result of homolytic N–C bond cleavage and abstraction of a hydrogen radical from the medium. Compounds III, V, and VIII could be formed by C–C and C–O bond cleavage and abstraction of a hydrogen atom from the solvent before rearrangement, as reported for N-arylcarbamates (Masilamani and Hutchins, 1976; Elad et al., 1965). Furthermore, analysis of an aqueous solution of I after irradiation at either 250 or 290 nm revealed V and VI; VI was identified as one of the major products by previous workers (Yao et al., 1989). The rearranged product VI could be explained by the mechanism proposed by Schwetlick et al. (1972) for a number of N-phenylcarbamates, whereby the N–C bond is cleaved to yield a solvent-cage radical pair and finally the photo-Fries product (Figure 4). The coupling constant of 7.8 Hz between the two aromatic protons in the NMR spectrum of the compound isolated from fraction 4 indicates that these are ortho to each other. The slightly broader signals of the resonances around δ 7.03 suggest further that this proton is next to a ring methyl group, with which it has very small long-range coupling. Obviously the symmetrical aromatic ring of compound X [Figure 1 (Yao et al., 1989)], where these protons are meta to each other, cannot be supported by this spectrum. If we make the assumption

that the ring methyl groups have not also rearranged in the photolysis, structure V is the only possibility for this compound.

The photo-Fries rearrangement almost always gives ortho or para substitution (Bellus, 1971). Where these positions are blocked, meta substitution is sometimes observed, and there are a very few reports of meta substitution even when the para position is not blocked (Lally and Spillane, 1991). Thus, although the formation of the meta-substituted product (V, Figure 1) is unusual, it is not surprising. What is surprising is our failure to isolate the expected para product (X, Figure 1), especially in light of the fact that earlier workers (Yao et al., 1989) observed X and not V. Metalaxyl does undergo rearrangement of the N-acyl group to the aromatic ring, but its predominant reactions are N-deacylation and elimination of the methoxycarbonyl group.

In consideration of the variety of compounds formed by the photodecomposition of metalaxyl in artificial sunlight and in the presence of humic acid, it appears to be reasonable to look for these compounds in soil and plants exposed to the fungicide.

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