# Identification of Sensitized Photooxidation Products of *s*-Triazine Herbicides in Water

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The dye-sensitized photodecomposition of *s*-triazine derivatives, commonly used as herbicides, has been studied. Aqueous, aerated solutions of these herbicides (ametryne, atraton, and atrazine), containing a sensitizer (riboflavin), were exposed to sunlight irradiation for several hours. The primary photo-degradation products formed were the deethylated *s*-triazines (a) and the oxidated product, 6-acet-amido-*s*-triazines (b). The yields of these products were for compounds a 55%, 62%, and 70% and for compounds b 2.6%, 3.0%, and 7.0% for the above herbicides, respectively. Further irradiation of the reaction mixtures led to the decomposition of compounds a and b with the formation of 4,6-diamino-*s*-triazine derivatives (c) which eventually photolyzed to unidentified compounds. The techniques used for isolation and identification of the above products were a combination of column chromatography, gas chromatography, and proton nuclear magnetic resonance, infrared, and mass spectrometry.

The use of sunlight dye-sensitized photodecomposition procedure for treatment of effluents has proven itself to be a promising technique (Acher, 1978; Acher and Saltzman, 1980; Acher et al., 1981; Saltzman et al., 1982).

The present work constitutes a study of the induced photodecomposition products of an important group of herbicides, *s*-triazines (Table I). These compounds, used as general or selective herbicides, are 4,6-bis(alkyl-amino)-*s*-triazines having an electrophilic substituent at
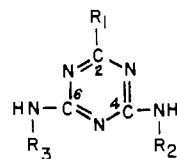
s-Triazine Derivatives

C-2. These herbicides are stable compounds and studies of their degradation have concerned themselves primarily with soil chemical degradation (Zimdahl et al., 1970). The hydrolysis of the R_1 substituent, leading to an inactive product, was studied in soil (Armstrong et al., 1967; Armstrong, 1968), and the findings were in agreement with data reported for water solutions (Wolfe et al., 1976). The direct photolysis of *s*-triazine herbicides in water and alcoholic solutions at 253.7 nm resulted in the nucleophilic displacement of the R_1 substituent and formation of hydroxyl and alkoxy derivatives, respectively (Pape and Zabik, 1972).

The sensitized photolysis of *s*-triazine herbicides in water was not investigated, probably because of their lack of reactivity toward singlet oxygen (Wolfe et al., 1976); this may be due in part to their alkylamino substituents which are known to quench singlet oxygen activity rapidly without reacting (Oannes and Wilson, 1968). The β values of *s*-triazine herbicides, representing their reactivities toward singlet oxygen, are higher than 37.5, predicting a very low reactivity (Foote, 1968; Wolfe et al., 1976). The direct photolysis of these compounds exposed to visible light is so low that it is not likely to have environmental importance.

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Table I. *s*-Triazine Derivatives Used in This Study

s-triazine	designation	R₁	R₂	R₃	concn,[a] ppm
ametryne	I	SCH₃	CH(CH₃)₂	CH₂CH₃	185
atraton	II	OCH₃	CH(CH₃)₂	CH₂CH₃	1800
atrazine	III	Cl	CH(CH₃)₂	CH₂CH₃	33
simazine	IV	Cl	CH₂CH₃	CH₂CH₃	5
propazine	V	Cl	CH(CH₃)₂	CH(CH₃)₂	8.6

[a] Water solubility at room temperature (Martin, 1972).

This paper describes the formation and the identification of the sensitized photodegradation products of *s*-triazine herbicides in water. The kinetic data concerning the photodecomposition reactions of *s*-triazine herbicides, the phytotoxicity bioassay of the reaction products, and other results of ecological importance will be reported separately.
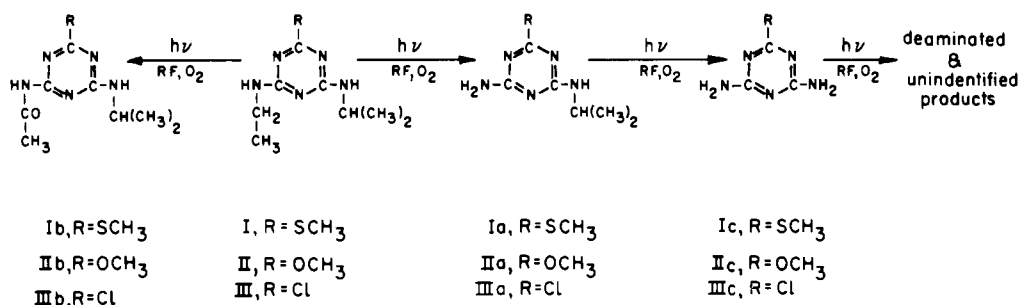
EXPERIMENTAL SECTION

Materials. The *s*-triazine herbicides used in this research, and listed in Table I, were used as water (deionized) solutions. Materials I, III, IV, and V (provided by Agan, Ltd., Israel) were chromatographically pure. Atraton (II) was prepared by refluxing an absolute methanolic solution (50 mL) of III (1 g), containing Na (0.090 g) overnight. To the cooled solution of II a few drops of acetic acid were added, the solution was evaporated in a Rotavapor, and the residue was crystallized from *n*-hexane to yield 0.9 g of pure II, mp 93–94 °C [lit. mp 94–95 °C (Melnikov, 1971)]. The H NMR and MS spectra correspond to the expected product.

The sensitizers methylene blue (MB) (BDH, No. 21632 Q), rose bengal (RB) (BDG, No. 2617.2E), riboflavin (RF) (BDH, No. 44088), and flavin mononucleotide (FMN) (BDH, No. 44089) were used as freshly prepared water (deionized) solutions (200 mg/L) or dissolved directly into the herbicide solutions before irradiation.

Irradiation. The photoreactions were carried out in graduated Pyrex cylinders with direct outdoors solar irradiation (from May to Sept 1981; altitude 100 m; latitude 32°N; longitude 34°50′E), or in a laboratory photoreactor equipped with an Osram-Power Star-HQI 400-W daylight lamp (Germany) mounted vertically and cooled by an air blower. The cylinders containing the solutions were arranged in a circle around the lamp and about 3 cm distant from it.

Scheme I

Ib, R=SCH$_3$	I, R = SCH$_3$	Ia, R=SCH$_3$	Ic, R = SCH$_3$
IIb, R=OCH$_3$	II, R = OCH$_3$	IIa, R=OCH$_3$	IIc, R=OCH$_3$
IIIb, R=Cl	III, R = Cl	IIIa, R = Cl	IIIc, R = Cl

Instrumentation. The gas chromatograph was a Tracor No. 506 instrument equipped with a Tracor No. 702 NP-detector and a glass column (1.2 m × 2 mm i.d.) filled with 3% OV-17 on Gas-Chrom Q 80–100 mesh. The gas carrier was dry N$_2$ (15 mL/min). The chromatograms were carried out isothermally at an oven temperature of 190 or 210 °C for the compounds II, III, IV, V, or I and their photoproducts, respectively. Electronic ionization (EI) and chemical ionization (CI) mass spectra (70 eV) were performed on a Du Pont No. 490 B low-resolution mass spectrometer, equipped with a dual EI/CI ion source (source temperature 190 °C; sample temperature 200 °C). High-resolution mass spectra were recorded on a Varian MAT No. 731 MS. The IR spectra were run on a Perkin-Elmer No. 257 instrument in KBr pellets. The H NMR spectra were carried out on a Varian FT-80A spectrometer (80 MHz) and all spectra are reported in δ from Me$_4$Si (internal standard). A Varian UV–vis spectrophotometer, Techtron No. 635, was used for spectrophotometric measurements. The light intensity in the 400–700-nm range was measured by a quantum sensor (Lambda Instrument Corp., Nebraska) connected to a digital integrator (Type TS 100A). The melting points were determined by using a Fisher Digital melting point analyzer, No. 355, and were not corrected.

Photodecomposition Procedure. Saturated aqueous solutions (500 mL) of s-triazine derivatives (Table I), containing a sensitizer (RF, MB, RB, or FMN) at different concentrations at an adjusted pH, were exposed to direct sunlight irradiation, (~2000 μEinsteins m^{-2} s^{-1}) or to day lamp irradiation in the photoreactor (~2400 μEinsteins m^{-2} s^{-1}). During the irradiation, air (water-washed) was flushed through an 0.1-mL pipet at the bottom of the solutions. The temperature of the solutions reached about 40 °C. Blank experiments (without sensitizers) were carried out with each series of experiments. The time of irradiation, depending on the purpose of the experiment (complete degradation of s-triazine or preparation of photoproducts), was determined by continuous sampling of the irradiated solutions and the injection of their ethyl acetate (EA) extracts to GC and spotting on TLC plates. The extracts were prepared by shaking the sample (1 mL) with ammonium sulfate (0.5 g) and EA (5 mL) in a stoppered test tube for ~30 s. The upper layer was further diluted with the same solvent to a final concentration of only a few ppm of triazine. This diluate was injected into the GC column (2 μL).

Isolation and Purification of the Photodegradation Products. For preparative purposes and quantitative estimation of the photoreaction products, concentrated solutions (~1000 ppm) of I, II, and III were prepared by dissolving the triazines (1.0 g) into ethyl alcohol (333 mL), to which deionized water (667 mL) containing RF (0.133 g) was added. The initial pH, before irradiation, was adjusted with 0.1 N HCl to 4.0 for the solution of I and II and to 2.0 for the solution of III, the progress of the re-

action was followed as above, and the irradiation was continued until about 90% of the starting materials were decomposed. After the irradiation, a sample of the solution (50 mL) was lyophilized (after removal of the ethyl alcohol in the Rotavapor). The dry residue obtained was dissolved in methanol (M)–dichloromethane (MC), 1:1 (10 mL), and the solution was spotted on TLC plate (aluminum sheets precoated with silica gel 60 G-254, Merck), eluted with M–MC, 1:20, and visualized by a 254-nm UV lamp or by iodine vapors. The same residue was used for MS (CI) analysis. Into the rest of the irradiated solution ammonium sulfate (25% w/v) was added, and the solution was extracted with EA (3 × 0.1 of the solution's volume). The extracts were combined and then dried over sodium sulfate, filtered, and evaporated to constant weight. The residue was submitted to column chromatography for preparative separation of different photodegradation products using a rapid chromatographic technique (Still et al., 1978). The elution was done with a mixture of MC–EA, 10:1.

RESULTS

The results of the photodecomposition of I, II, and III, reported below, are from experiments carried out with concentrated aqueous ethanolic solutions (1000 ppm). The sensitizer used in these experiments was RF at a pH which was found to give the fastest photodecomposition rate.

Irradiation of aqueous solutions of s-triazine derivatives (I, 200 ppm; II, 200 ppm; III, 30 ppm) in the presence of RF (0.1 mol of RF/mol of triazine) at various pHs gave the same photoreaction products as the above concentrate solutions used for preparative purposes (Scheme I).

The efficiency of other sensitizers like MB, RB, and FMN in the photodecomposition of s-triazine derivatives at various pHs (8.2, 7.0, and 4.0) and concentrations (2, 5, and 10 ppm) was checked too. The sensitizers MB and RB did not cause any significant decrease in the herbicide concentrations. Alternatively, the FMN gave results similar to those of RF under the same working conditions.

Blank experiments (without sensitizer) did not show any decrease in the concentrations of I, II, and III in the irradiated solutions. The experiments performed under nitrogen atmosphere (with RF) yielded only minute amounts of the deethylated product (a).

Irradiation of saturated solutions of IV and V (pH 4.0, 0.3 mol of RF/mol of IV or V, for 1 h) showed a higher rate of photoreaction for IV (25% N-deethylation reaction) than for V (12% N-deisopropylation reaction).

The photoreaction oxidated products (b) can be obtained also by acetylation (pyridine–acetic anhydride) of compound a; the products (c) can be obtained also by irradiation of aqueous solution of compound a (Scheme I).

The irradiation of the reaction mixtures, done either by sunlight outdoors or by daylight lamp in the photoreactor, led to the same photodecomposition products, but the

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Table II. High-Resolution MS, Significant Peaks, and Major Fragmentation of Photodecomposition Products of I

pro-duct	mass found	% abundancy	C	H	N	O	S	structure
I$_a$	199.0934	100.00	7	13	5		1	M$^+$
	184.0629	89.09	6	10	5		1	M$^+$ $-$ CH$_3$
	157.0453	39.70	4	7	5		1	M$^+$ $-$ CH$_3$CH=CH$_2$
	127.0048	6.29	3	3	4		1	M$^+$ $-$ C$_4$H$_{10}$N
	111.0803	12.30	3	5	5			M$^+$ $-$ C$_4$H$_{10}$S
	110.0688	13.73	3	4	5			M$^+$ $-$ C$_4$H$_9$S
I$_b$	241.0992	100.00	9	15	5	1	1	M$^+$
	226.0690	32.99	8	12	5	1	1	M$^+$ $-$ CH$_3$
	199.0847	8.18	6	9	5	1	1	M$^+$ $-$ C$_3$H$_6$
	198.0899	8.27	7	12	5		1	M$^+$ $-$ C$_2$H$_3$O
	184.0638	54.51	7	12	4		1	M$^+$ $-$ C$_2$H$_3$NO
	157.0437	14.91	4	7	5		1	M$^+$ $-$ C$_5$H$_8$O
	110.0355	7.81	3	4	5			M$^+$ $-$ C$_6$H$_{11}$OS
I$_c$	157.0401	100.00	4	7	5		1	M$^+$
	156.0332	9.41	4	6	5		1	M$^+$ $-$ H
	111.0523	37.62	3	5	5			M$^+$ $-$ SCH$_2$
	69.0323	26.96	2	3	3			M$^+$ $-$ C$_2$H$_4$N$_2$S
	68.0242	11.65	2	2	3			M$^+$ $-$ C$_2$H$_5$N$_2$S

reaction rate was somewhat faster in the experiments performed in the photoreactor (used for preparative purposes).

Identification of the Photoreaction Products of I. TLC analysis of the residue obtained after lyophilization of the irradiated solution (1000 ppm, pH 4.0, 4 h) showed one main product, R_f = 0.43, corresponding to Ia. Weaker spots appeared at R_f = 0.69, R_f = 0.59, and R_f = 0.18, corresponding to I, Ib, and Ic, respectively. At R_f = 0.29 a fluorescent spot, derived from the photodecomposition of RF, was seen; the same spot appeared in the irradiated solution of RF alone. The GC analysis of the EA extract indicated a ratio of about 8:1 for Ia:I (I, t_R = 3.8 min; Ia, t_R = 2.9 min). Small peaks were seen for Ib (t_R = 7.0 min) and for Ic (t_R = 2.2 min). The direct probe MS (CI) spectra of the residue after lyophilization indicated six protonated molecular ions (M$^+$H) corresponding to I (228), Ia (200), Ib (242), Ic (158), Id (127, 2-(methylthio)-s-triazine), and Ie (119, 2-mercapto-s-triazine).

2-(Methylthio)-4-(isopropylamino)-6-amino-s-triazine *(Ia)*. This compound was isolated from the irradiated reaction mixture of I by column chromatography in 55% yield. Crystallization from benzene gave needles with mp 112–113 °C [lit mp 114–116 °C (Yamamoto and Namerikawa, 1964)]. The NMR spectrum of Ia, compared with that of I, indicated the disappearance of the signals at δ 1.11 (t, J = 7.2 Hz, 3 H, CH$_2$CH$_3$) and 3.40 (m, 2 H, CH$_2$CH$_3$), corresponding to the ethyl group. Other signals were almost without any changes: δ 2.44 (s, 3 H, SCH$_3$), 1.19 [d, J = 6.5 Hz, 6 H, CH(CH$_3$)$_2$], and 4.15 [m, 1 H, CH(CH$_3$)$_2$].

The significant peaks in the high-resolution MS of Ia are presented in Table II. Decomposition of the molecular ion (m/e 199) occurred through elimination of the isopropyl group via a cyclic McLafferty rearrangment (Safe and Hutzinger, 1973) to yield the m/e 157 ion. This ion expelled SCH$_3$ to give the m/e 110 ion. In addition, the molecular ion eliminated also a methyl group (m/e 184).

2-(Methylthio)-4-(isopropylamino)-6-acetamido-s-triazine *(1b)*. This compound is a minor product of the photoreaction and was isolated from the irradiated mixture, by column chromatography, in 2.6% yield. Crystallization from ethyl acetate gave white needles with mp 183–184 °C. NMR spectra show, besides, the signals corresponding to the isopropyl group [δ 1.24 (d, J = 6.5 Hz, 6 H) and 4.17 (m, 1 H)] and the SCH$_3$ group [δ 2.48 (s, 3 H)], a new signal [δ 2.62 (s, 3 H)] corresponding to

the acetyl group. High-resolution MS of Ib (see Table II) indicated decomposition of the molecular ion through elimination of CH$_3$, C$_3$H$_6$, CH$_3$CO, and CH$_3$CON groups with formation of the m/e 226, 199, 198, and 184 ions, respectively. Further fragmentation of the m/e 199 ion gave the m/e 157 and m/e 110 species through stepwise elimination of CH$_3$CO and SCH$_3$ groups. The IR spectra of the Ib confirmed the presence of an amide group at 1670 cm^{-1}.

2-(Methylthio)-4,6-diamino-s-triazine *(Ic)*. Ic is a secondary product of the photoreaction, formed through the photodecomposition of Ia. It was isolated from the irradiated aqueous solution of Ia (250 ppm, pH 4.0, 6 h), by extraction with EA. Crystallization from EA of the residue obtained by evaporation of the extract afforded Ic in 13% yield, mp 269–271 °C [lit. mp 270–272 °C (Welcher et al., 1959)]. The NMR spectrum of Ic (in a mixture of CDCl$_3$ and MeOD) showed the methylthio signal [δ 2.45 (s)]. High-resolution MS (Table II) of Ic indicated elimination of SCH$_2$ from the molecular ion. The resultant ion (m/e 111) decomposed further by elimination of two moles of hydrogen cyanide (m/e 69).

Identification of the Photoreaction Products of II. TLC analysis of the residue obtained from the irradiated reaction mixture of II (1000 ppm, pH 4.0, 7 h) indicated a major spot at R_f = 0.30 (IIa) and two minor spots at R_f = 0.55 (unreacted II) and R_f = 0.50 (IIb). GC analysis of the ethyl acetate extract showed a ratio of about 2.5:1 for IIa:II (II, t_R = 3.7 min; IIa, t_R = 2.7 min). Two other minor peaks were seen at t_R = 8.3 min (II$_b$) and t_R = 2.2 min (IIc). The direct probe MS (CI) spectra of the residue after lyophilization indicated five protonated molecular ions corresponding to II (212), IIa (184), IIb (226), IIc (142), and IId (98, 2-hydroxy-s-triazine).

2-Methoxy-4-(isopropylamino)-6-amino-s-triazine *(IIa)*. This is the major photolysis product which was isolated from the irradiated mixture of II by column chromatography in 62% yield. Crystallization from benzene afforded crystals with mp 99–101 °C. NMR data were δ 1.20 [d, J = 6.4 Hz, 6 H, CH(CH$_3$)$_2$], 3.87 (s, 3 H, OCH$_3$), and 4.10 [m, 1 H, CH(CH$_3$)$_2$]. MS (CI) spectra showed an m/e 184 ion corresponding to the protonated molecular ion of IIa.

2-Methoxy-4-(isopropylamino)-6-acetamido-s-triazine *(IIb)*. This compound was isolated from the irradiated mixture of II, by column chromatography in 3% yield. Crystallization from ethyl acetate afforded crystals with mp 151–152 °C. NMR data were δ 1.24 [d, J = 6.5 Hz, 6 H, CH(CH$_3$)$_2$], 3.95 (s, 3 H, OCH$_3$), 4.15 [m, 1 H, CH-(CH$_3$)$_2$], and 2.62 (s, 3 H, COCH$_3$). IR spectra of IIb confirmed the presence of the amide group at 1680 cm^{-1}. MS (CI) spectra showed an m/e 226 ion corresponding to the protonated molecular ion of IIb.

2-Methoxy-4,6-diamino-s-triazine *(IIc)*. This compound was detected (<1%) in the residue obtained after the lyophilization of the irradiated mixture of IIa (250 ppm, pH 4, 3 h) by MS (CI). The spectra showed the protonated molecular ions at m/e 184 and m/e 142 which can be attributed to the unreacted IIa and to IIc.

Identification of the Photoreaction Products of III. TLC analysis of the residue of the irradiated reaction mixture (800 ppm, pH 2, 5 h) showed mainly one spot at R_f = 0.40, corresponding to IIIa. Weak spots were seen at R_f = 0.62, 0.52, and 0.12 corresponding to III, IIIb, and IIIc, respectively. GC analysis indicated a ratio of 5:1 for IIIa:III (III, t_R = 4.5 min; IIIa, t_R = 3.5 min). At t_R = 7.0 min and t_R = 2.9 min, small peaks appeared corresponding to IIIb and IIIc, respectively. MS (CI) spectra of the residue after lyophilization showed protonated molecular

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ions corresponding to III (216), IIIa (188), IIIb (230), IIIc (146), IIId (114, 2-chloro-s-triazine), and IIIe (154, 4-(isopropylamino)-6-amino-s-triazine).

2-Chloro-4-(isopropylamino)-6-amino-s-triazine (IIIa). This compound is the main product in the photodegradation of III, and it was isolated from the irradiated mixture by column chromatography in 70% yield. Crystallization from benzene gave crystals with mp 134 °C [lit. mp 134-136 °C (Gysin and Knüli, 1960)]. NMR data were δ 1.20 [d, J = 6.5 Hz, 6 H, CH(CH_3)$_2$] and 4.10 [m, 1 H, CH(CH$_3$)$_2$]. MS (CI) showed an m/e 188 corresponding to the M⁺H ion of IIIa.

2-Chloro-4-(isopropylamino)-6-acetamido-s-triazine (IIIb). This compound is a minor product of the photolysis of III and was isolated from the irradiated mixture by column chromatography in about 7% yield. Crystallization from ethyl acetate afforded crystals with mp 187-188 °C. NMR data were δ 1.25 [d, J = 6.5 Hz, 6 H, CH(CH_3)$_2$], 2.58 (s, 3 H, COCH$_3$), and 4.10 [m, 1 H, CH(CH$_3$)$_2$]; MS (CI) showed an m/e 230 corresponding to the M⁺H ion of IIIb. The IR spectra of IIIb confirmed the presence of an amide group at 1690 cm⁻¹.

2-Chloro-4,6-diamino-s-triazine (IIIc). This compound was detected (<1%) in the residue obtained after the lyophilization of the irradiated mixture of IIIa (250 ppm, pH 2, 3 h) by MS (CI). The spectra showed protonated molecular ions at m/e 188 and m/e 146 which can be attributed to the unreacted IIIa and the title compound IIIc.

DISCUSSION

The identification of the photodegradation products (a–c and others) made it possible to deduce the pattern of the pathways which are followed in the sensitized photodecomposition of the s-triazine herbicides (Scheme I). The first and the major photodegradation product which was detected in the irradiated solutions was an N-deethylated compound (a). Simultaneously, a minor oxidated compound (b) was formed. Further irradiation resulted in the decrease of the amount of compound a and b and appearance of the product c, which has a complete N-dealkylated structure (Scheme I). Additional irradiation decomposed this product too, probably leading to the formation of the deaminated compound (d). This was detected only by MS (CI) analysis of the residue obtained by lyophilization of the reaction mixture, which eventually was decomposed to unidentified compounds. Other compounds were found in minute amounts only, and their structures were assigned by MS (CI) direct probe analysis and are not considered in this discussion.

It should be noted that the reported photohydrolysis of s-triazines, with the formation of 2-hydroxy derivatives (Pape and Zabik, 1972), was not observed in any of the above experiments, even after exposure for several days to sunlight or daylight lamp irradiation.

The rate of photoreactions was affected by the electronegativity of the substituent at C-2, which interferes through the aromatic ring with the stability of the substituents at C-4 and C-6. This might explain the following decrease observed in the reaction rate: -SCH$_3$ > -OCH$_3$ > -Cl. For example, under the same experimental conditions (30 ppm, 0.3 mol of RF/mol of triazine, pH 4, 1 h), the amount of triazines decomposed was 83%, 59%, and 35% for the compounds I, II, and III, respectively.

The rate of reaction was also affected by the pH of the reaction mixture. The increase in the rate of reaction by lowering the pH of the reaction mixture can be explained by an increase in the hydrogen abstraction ability of RF at a pH lower than neutral. However, the photodecom-
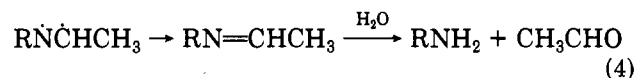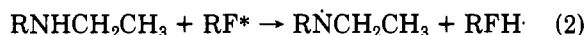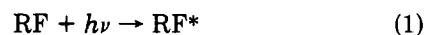
position reactions carried out under neutral or alkaline conditions led to the same degradation products.

In all the s-triazines irradiated, the N-ethyl group (at C-6) was found to be photolyzed *prior* to the isopropyl group (C-4). The lower ionization potential of the amine (at C-4) adjacent to the methyne group compared with the amine (at C-6) adjacent to the methylene group might explain this observation. Considerations of the stability of the different possible N-ethyl and N-isopropyl radicals which can take part in the reaction also support this explanation.
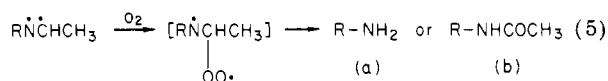
The higher photodecomposition rate of compound IV, compared with that of compound V, was in good agreement with the above.

A similar pathway of N-dealkylation of s-triazines—first the N-ethyl group, followed by the removal of the N-isopropyl group—was found to be the biochemical degradation mechanism generally valid for all biological systems examined thus far (Kearney and Kaufman, 1969).

The mechanism of photosensitized decomposition of s-triazines was thought likely to occur via photooxidation mediated by excited-state complexes or "exciplexes" (Wolfe et al., 1976; Bowman et al., 1974; Wagner and Kemppainen, 1969), since alkylamino groups are particularly prone to photoreact in this way (Cohen, 1973). This pathway consists of the oxidation of amine and the reduction of the sensitizer via an electron transfer within the exciplex. An alternative mechanism can be described by the following sequence of reactions, in which hydrogen is abstracted from the amine by excited RF (eq 2). Another molecule of RF is used for a second hydrogen abstraction (eq 3) with the formation of aldimine, which is readily hydrolyzed to the corresponding N-deethylated products (a) and acetaldehyde, which indeed was detected in the irradiated solution by using the Schiff's reagent and the p-nitrophenylhydrazine methods (Vogel, 1961).

$$RF + h\nu \rightarrow RF^* \qquad (1)$$

$$RNHCH_2CH_3 + RF^* \rightarrow R\dot{N}CH_2CH_3 + RFH \cdot \quad (2)$$

$$R\dot{N}CH_2CH_3 + RF^* \rightarrow R\dot{N}CHCH_3 + RFH \cdot \quad (3)$$

$$R\dot{N}CHCH_3 \rightarrow RN{=}CHCH_3 \xrightarrow{H_2O} RNH_2 + CH_3CHO \qquad (4)$$

The presence of oxygen in the irradiation mixture was found to be essential for the photodecomposition reaction. Only minute amounts of the main photodegradation products (a) were formed when oxygen was flushed out from solutions with nitrogen. This phenomenon suggests the possible participation of hydroperoxide radicals in the photoreaction mechanism. The radical (eq 3), which formed by RF* hydrogen abstraction from the amine (at C-6), could be expected to react with the dissolved oxygen from solution to yield the hydroperoxide radical (eq 5) (Schaefer and Zimmermann, 1970):

$$R\dot{N}CHCH_3 \xrightarrow{O_2} \underset{\underset{OO\cdot}{|}}{[R\dot{N}CHCH_3]} \longrightarrow \underset{(a)}{R{-}NH_2} \text{ or } \underset{(b)}{R{-}NHCOCH_3} \quad (5)$$

This radical might, in turn, lead to the formation of the amines (a) or of the amide products (b).

An additional possible way of herbicide degradation might result from the hydroperoxide radicals formed in the regeneration of RF from RFH (6):

$$RFH \cdot + O_2 \rightarrow RF + HOO \cdot \qquad (6)$$
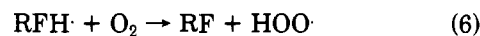
This regeneration of RF is evident from the fact that less than the stoichiometric amount of it is required for com-

plete decomposition of s-triazines.

ACKNOWLEDGMENT

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Metabolism of an Acaricide, 4-Methyl-3-(n-propylthio)phenyl 4-Nitrophenyl Ether, in Rat

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[14]C-Labeled 4-methyl-3-(n-propylthio)phenyl 4-nitrophenyl ether (MPNE) was administered orally to rats at a dosage of 400 mg/kg of body weight. Near-maximum elimination was achieved within 4 days. At the end of 20 days, approximately 56% of radioactivity was found in feces and 27% in the urine. At the same time, a low level of radioactive residue was found mainly in the adipose tissue in the form of the original parent compound. The metabolism of the acaricide is mainly carried out by the mixed-function oxidase. In addition to the parent compound, two major metabolites γ-hydroxy fulfoxide ether and sulfoxide ether were found in feces. One minor metabolite was identified as γ-hydroxy sulfone ether besides a few unknown minor polar metabolites. In urine only γ-hydroxy sulfoxide ether was identified, though there were several other unknown polar metabolites. No conjugated products were found to exist in the feces or urine. While no amino derivative of MPNE was found among in vivo metabolic products, an amino derivative of MPNE sulfoxide was found to form in vitro. This reductive metabolism is stimulated by the presence of NADPH and is apparently coupled with mixed-function oxidase.

MPNE [4-methyl-3-(n-propylthio)phenyl 4-nitrophenyl ether] is a new type of specific acaricide of which chemical structure is quite different from any other acaricide being used today. It has shown promise for control of mites such as Tetranychus urticae and Panonychus citri (Kato et al., 1975). The most intriguing aspect of this acaricide is that

it is a diphenyl ether compound that was originally intended for a herbicide. Instead, the compound has shown an excellent acaricidal activity without any appreciable herbicidal actions. As a result, many questions may be raised as to its mode of action, metabolism, and biological effects. One of the first questions scientists could ask is the nature of the actual toxic principle to animals, whether it is the starting compound or its metabolites. Another important question is how it is metabolized and whether any of its metabolic products accumulate in biological

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