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Photodecomposition of Sustar in Water

Glenn C. Miller[1] and Donald G. Crosby*

Aqueous solutions of the plant growth regulator Sustar were unstable in sunlight. Sustar (pK = 4.5) exists largely in ionized form in typical environmental solutions, and its sunlight photodegradation rate in pH 3.4 buffer was three times that at pH 7.2 even though the UV absorbance of the ionized Sustar is the greater. The primary photoproduct was 5-methyl-2-acetamido-1,4-benzoquinone (IV), formed by oxidation of a sulfonanilide radical to 1-(1,1,1-trifluoromethanesulfonimido)-2-methyl-5-acetamido-1,4-benzoquinone followed by hydrolysis to IV and trifluoromethanesulfonamide. Other photoproducts, formed via an anilino radical, included *N*-(3-amino-4-methylphenyl)acetamide, the corresponding nitro compound *N*-(4-methyl-3-nitrophenyl)acetamide, a sulfur dioxide extrusion product, *N*-[3-(*N*-trifluoromethylamino)-4-methylphenyl]acetamide, and *N*-(3-amino-4-formylphenyl)acetamide. Carbon dioxide formation indicated that extensive ring oxidation also occurred. Irradiation with a mercury arc produced two additional products, identified as *o*- and *p*-aminosulfones corresponding to photo-Fries rearrangement products. Sunlight irradiation of [^{14}C]Sustar in natural water provided a degradation rate greater than that in buffer, but no extractable photoproducts were observed. The terminal residues included colored polar substances, carbon dioxide, and trifluoromethanesulfonic acid and its amide.

Sustar, *N*-[3-[(1,1,1-trifluoromethylsulfonyl)amino]-4-methylphenyl]acetamide (I), is a growth regulator which has shown activity in controlling both grasses and broadleaf plants. Sustar is acidic (pK = 4.5), due to its trifluoromethylsulfonyl group, and is formulated as the diethanolamine salt. Substituted sulfonanilides also have come under investigation for their herbicidal properties (Trepka et al., 1974).

As part of a continuing study on the photochemical fate of pesticides, we were interested in examining a representative sulfonanilide; no previous work has been published on the environmental photochemistry of this group of compounds. As Sustar is acidic, we also wished to investigate the effect of pH on its photodegradation rate and photoproduct distribution.

EXPERIMENTAL SECTION

Materials. Technical Sustar (87% pure; 3M Company, St. Paul, Minn.) was recrystallized three times from 95% ethanol, with charcoal decolorization, until homogeneous on thin-layer chromatography (TLC) and gas chromatography (GLC), mp 180.5–182 °C. Standards of *N*-(3-amino-4-methylphenyl)acetamide (VI), *N*-(4-methyl-3-nitrophenyl)acetamide (VIII), and *N*-(3-amino-6-methylphenyl)-1,1,1-trifluoromethanesulfonamide (IX) were provided by 3M Company and used as received.

N,N-Dimethyltrifluoromethanesulfonamide (V) was prepared by adding trifluoromethanesulfonyl chloride (Aldrich Chemical Company) to solid ammonium carbonate, followed by methylation with ethereal diazomethane. Mass spectrum, m/e 177 (M^+), 108 ($M^+ - CF_3$, base).

5-Methyl-2-acetamido-1,4-benzoquinone (IV) was prepared by addition of 6-amino-*m*-cresol (10 g) to a solution of 40 mL of acetic anhydride in 50 mL of ethyl acetate. The mixture was stirred for 2 h, the solvent was removed by evaporation, and 2 equiv of aqueous sodium hydroxide was added. After standing overnight, the solution was acidified to pH 5 and the precipitated phenol removed by filtration. Oxidation to the quinone was accomplished by addition of the crude 6-acetamino-*m*-cresol to sodium dichromate (55 g) in 300 mL of glacial acetic acid at 0 °C (Emerson and Smith, 1940). The solution was stirred for 2 h, diluted with 200 mL of water, extracted with six 150-mL portions of chloroform, and the organic layer reextracted with 200 mL of 0.1 N NaOH and evaporated to dryness. Recrystallization from methanol gave orange crystals: mp 191–192.5 °C; mass spectrum, m/e 179 (M^+), 137 ($M^+ - CH_2CO$), 109 ($M^+ - CH_2CO - CO$); NMR spectrum ($CDCl_3$), δ 8.2 (s, NH), 7.6 (s, CH),

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2.3 (s, CH_3), 2.1 (s, CH_3); UV spectrum (methanol), λ_{max} 380 nm, 268 nm.

1-(1,1,1-Trifluoromethanesulfonimido)-2-methyl-5-acetamido-1,4-benzoquinone (II) was synthesized and partially purified by the procedure (Richter and Dresseler, 1962) for the synthesis of 1-benzenesulfonimido-1,4-naphthoquinone. A suspension of Sustar (5 g) in 33 mL of glacial acetic acid was stirred while 60 g of lead tetraacetate was added in small portions over 45 min. The reaction mixture was heated to 45 °C for 1 h, after which 2 mL of propylene glycol was added to destroy excess lead tetraacetate. The solution was poured into 2 L of water, neutralized with base, and extracted with three 400-mL portions of chloroform. The organic layer was back-extracted with pH 7.5 phosphate buffer and the organic layer dried over sodium sulfate and evaporated to an oil. GLC–mass spectral analysis indicated the presence of II as the principal product: *m/e* 310 (M^+), 268 ($M^+ - CH_2CO$), 177 ($M^+ - SO_2CF_3$), 163 ($M^+ - NSO_2CF_3$), 135 ($M^+ - SO_2CF_3$, CH_2CO), 121 ($M^+ - NSO_2CF_3$, CH_2CO). However, other products also were present, particularly the quinone hydrolysis product IV, and attempts at further purification of II were unsuccessful.

Uniformly ring-labeled [^{14}C]Sustar (sp act. 2796 dpm/μg) was provided by the 3M Company. It was homogeneous on TLC and used as received.

Irradiation and Analysis. Sustar (100 mg/L, 3.4×10^{-4} M) was dissolved in a 10^{-3} M solution of disodium phosphate, the pH was adjusted to either 7.2 or 3.6 with acid, and irradiation was conducted in a preparative photoreactor (Crosby and Tang, 1969) with a Westinghouse FS40 blacklight (λ_{max} 310 nm). The solution temperature was controlled by circulating 20 °C water through flexible plastic tubing wrapped around the reaction chamber, and filtered air was passed through the solutions at 10 mL/min to maintain air saturation. The exit port of the photoreactor was fitted with a 6 cm × 1 cm column containing Amberlite XAD-4 resin (Rohm and Haas Company) which has been shown (Singmaster, 1975) to effectively trap volatile organic compounds from air.

Outdoor irradiations were conducted during the months of May through September. Similar experiments during the winter months were hampered by the diminished solar ultraviolet energy (Koller, 1965) (Figure 1) which afforded only very slow degradation rates. In all cases, dark controls were run at a temperature the same as those of the corresponding photolysis, and in outdoor irradiations the control flasks were covered with aluminum foil and placed near the flasks containing the irradiated solutions.

Sunlight photolysis rates were measured (August) at pH 7.2 and 3.6 and replicated. Samples (20 mL) were taken at appropriate time intervals and analyzed (Eisenbraun et al., 1970) by acidification to pH 2 followed by extraction into 10 mL of ethyl acetate. Ethereal diazomethane was added and after 15 min the extract was transferred to a centrifuge tube and evaporated under nitrogen to 1 mL, and the methylated Sustar was analyzed by GLC at 220 °C (recoveries 95–103%).

Radiolabeled Sustar (4.0×10^{-6} M) was irradiated at pH 3.6 and 7.2 with the FS40 lamp, samples were collected and lyophilized, and the residue was taken up in methanol and its components separated on TLC. Bands corresponding to the previously identified photoproducts were scraped into vials and counted directly in 5 mL of water and 15 mL of PCS solubilizer. [^{14}C]Sustar also was exposed to August sunlight in pH 8.6 water obtained from a creek adjacent to the University of California, Davis campus; labeled Sustar in methanol was added to the water to provide a concentration of 2.0×10^{-6} M. Samples were taken at 9 and 17 days and extracted with dichloromethane as before. Each extract was evaporated under nitrogen to a volume of 200 μL, half spotted on TLC plates and developed in ethyl acetate–benzene–acetic acid (90:60:1, v/v) for counting of individual bands, and the other half was counted directly by liquid scintillation.

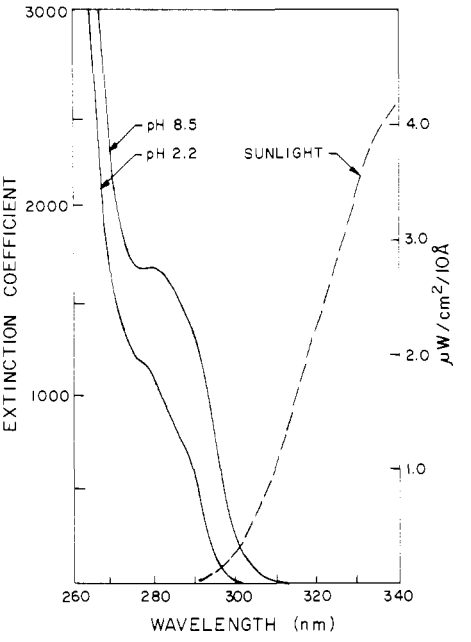


Figure 1. Ultraviolet absorption spectra of Sustar.

Isolation and Identification. One-liter portions of irradiated solutions were adjusted to pH 7.0 and extracted with three 250-mL portions of chloroform, acidified, and again extracted three times with 250 mL of chloroform. The two combined extracts were evaporated to near dryness, transferred to centrifuge tubes, evaporated to 200 μL, spotted on TLC plates, and developed as described. Bands were detected by color or by fluorescence-quenching under 254-nm light, collected, and extracted with chloroform–methanol, and their physical and chemical properties were examined. Unchanged Sustar generally was the principal constituent, but it remained in the neutral aqueous phase.

Mass spectra were obtained with a Finnigan Model 3000 Peak Identifier and a 150 × 0.3 cm column containing 1% OV-1 on 80–120 mesh Gas-Chrom Q (helium flow 10 mL/min, ionization voltage 70 eV). Infrared (IR) spectra were recorded on a Perkin Elmer Model 337 infrared spectrophotometer in KBr pellets, ultraviolet (UV) absorption spectra of aqueous Sustar solutions on a Cary 15 spectrophotometer, and nuclear magnetic resonance (NMR) spectra on Varian A60 or JEOL PS-100 FT-NMR spectrometers in $CDCl_3$. GLC separations were performed on a Varian 2400 gas chromatograph equipped with a flame ionization detector and 150 × 0.3 cm i.d. glass column containing 3% OV-17 on 100–120 mesh Gas-Chrom Q (injection port and detector temperatures 250 and 275 °C, respectively; N_2 flow 35 mL/min). TLC separations were performed on commercial (Brinkman) 20 × 10 cm glass plates coated with 0.25 mm silica gel G containing zinc orthosilicate phosphor.

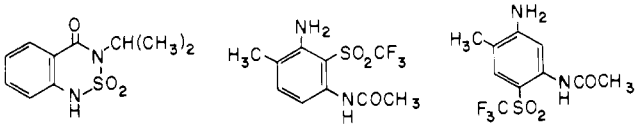
Radioactive TLC spots were detected with either a Berthold LB 2747 Radiochromatogram Scanner or Kodak X-Omate R autoradiography film. Liquid Scintillation counting (Packard Tri-carb) of aqueous samples was conducted in PCS solubilizer (Amersham-Searle) with quench correction by internal standard.

Table I. Properties of Sustar Photolysis Products

R_f[a]	ET,[b] °C or other	mass spectrum	proposed structure
0.39	264	296 (M^+), 254 ($M^+ - CH_2CO$), 163 ($M^+ - SO_2CF_3$), 121 ($M^+ - CH_2CO - SO_2CF_3$)	I[d]
0.28	235	310 (M^+), 268 ($M^+ - CH_2CO$), 177 ($M^+ - SO_2CF_3$), 135 ($M^+ - CH_2CO - SO_2CF_3$)	II[d]
0.53	195	179 (M^+), 137 ($M^+ - CH_2CO$), 109 ($M^+ - CH_2CO - CO$)	IV[d]
	80[e]	177[c] (M^+), 108 ($M^+ - CF_3$)	V[d]
0.14	230	164 (M^+), 122 ($M^+ - CH_2CO$), 121 ($M^+ - CH_2CO - H$), 105 ($M^+ - CH_2CO - H - NH_2$)	VI[d]
0.24	202	232 (M^+), 190 ($M^+ - CH_2CO$), 175 ($M^+ - CH_2CO - NH$), 105 ($M^+ - CH_2CO - CF_3NH$)	VII
0.30	235	194 (M^+), 177 ($M^+ - OH$), 152 ($M^+ - CH_2CO$), 135 ($M^+ - CH_2CO - OH$)	VIII[d]
0.43	236	254 (M^+), 121 ($M^+ - SO_2CF_3$), 105 ($M^+ - SO_2CF_3 - NH_2$)	IX[d]
0.26	242	178 (M^+), 150 ($M^+ - CO$), 136 ($M^+ - CH_2CO$), 108 ($M^+ - CH_2CO - CO$)	X
0.18	195	162 (M^+), 161 ($M^+ - H$), 93 ($M^+ - CNCOCH_3$)	XI
	60[e]	164[c] (M^+), 69 ($M^+ - SO_3CH_3$)	XII[d]
0.56	221	190 (M^+), 175, 105	XIII?

[a] Ethyl acetate-acetic acid (90:60:1). [b] Elution temperature, program from 120 °C at 12 °C/min. [c] Methylated. [d] Structure confirmed by comparison with authentic standards. [e] Isothermal.

Mercury Arc Irradiation of Sustar in Water. Sustar (50 mg) in 5 mL of methanol was added to 500 mL of phosphate buffer (10^{-2} M, pH 7.5). The solution was irradiated in a photoreactor fitted with a Hanovia medium-pressure mercury arc (immersion type) for 6 h in the presence of air and extracted twice with 200 mL of chloroform, and the organic phases were evaporated to 1 mL. GLC indicated a complex mixture containing four major constituents, two of which were identified as the quinone IV and unreacted Sustar. The other two major products, XV and XVI, were isolated by TLC at R_f 0.54



XIV XV XVI

and 0.56 (1:1 acetone–hexane), and milligram quantities were obtained by collection from preparative GLC (F&M Model 720 with thermal conductivity detector, 60 × 0.6 cm i.d. column containing 5% SE-30 on DCMS Chromosorb W), and their purity was confirmed by reinjection on a different column (2% OV-101 on Gas-Chrom Q). Both were electron-capturing and not acidic.

Compound XV. Mass spectrum *m/e* 296 (M^+), 254 ($M^+ - CH_2CO$), 227 ($M^+ - CH_3$), 163 ($M^+ - CF_3SO_2$), 121 $M^+ - CF_3SO_2 - CH_2CO$); IR (KBr pellet) 3530, 3400 (amine), 1630 (amide carbonyl), 1350 cm^{-1} (sulfone); NMR ($CDCl_3$) δ 2.16 and 2.18 singlets (6 H, methyl), 5.65 broad singlet (amine), 2.0 broad singlet (amide), 7.2–7.7 quartet (2 H, aromatic).

Compound XVI. Mass spectrum *m/e* 296 (M^+), 254 ($M^+ - CH_2CO$), 227 ($M^+ - CF_3$), 163 ($M^+ - CF_3SO_2$), 121 ($M^+ - CF_3SO_2 - CH_2CO$); IR 3520 and 3410 (amine), 1620 (amide carbonyl), 1340 cm^{-1} (sulfone).

RESULTS AND DISCUSSION

Although Sustar solutions absorb only weakly in the solar spectrum (Figure 1), the compound was degraded in sunlight at moderate rates (Figure 2). The UV absorption spectra (Figure 1) indicated a pronounced difference in absorptivity depending on whether Sustar is ionized (pH 8.5) or unionized (pH 2.2). The degradation rates in sunlight also depended on pH; although absorption was greatest at a pH where Sustar is ionized, degradation was only one-third as rapid compared to acidic conditions.

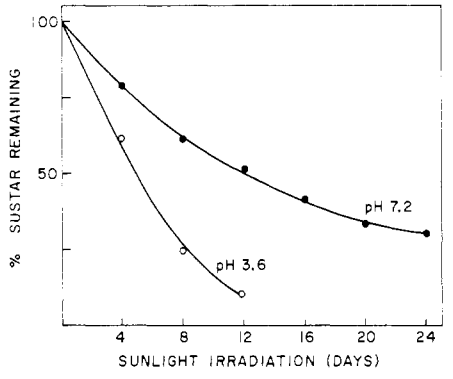


Figure 2. Photodegradation rates of 3.4×10^{-4} M aqueous Sustar.

Acidic Photolysis. Irradiation of 3.4×10^{-4} M aqueous Sustar at pH 3.6 with the FS40 lamp produced a yellow color within 1 h due to the quinone IV, the major photoproduct. The sulfur dioxide extrusion product VII, the amine VI, and trifluoromethanesulfonamide (V) also were present in significant quantities. Minor photoproducts included II, IX, X, and XI, each representing less than 5% of IV. Prolonged irradiation resulted in colorless solutions containing no extractable photoproducts.

Whenever possible, photoproduct structures were established by comparison of chromatographic properties and mass spectra with those of authentic standards (Table I). However, the identities of compounds VII, X, and XI were based on physical and chemical properties alone. Each of these gave a discernible molecular ion; the $M^+ - 42$ ion, indicative of the acetamide group, was observed in VII and X, and the quinoid compound XI lost the imide portion of the molecule (Budzikiewicz et al., 1967). The $M^+ - 133$ ion was diagnostic for the presence of SO_2CF_3.

The base peak of XI was *m/e* 93, equivalent to loss of $C{=}NCOCH_3$. The strong $M^+ - 1$ peak was consistent with an aromatic amine and reaction with acetic anhydride produced a compound with the expected parent *m/e* 204. IR spectra also indicated amine (3420 and 3470 cm^{-1}) and conjugated carbonyl (1694 cm^{-1}), although no $M^+ - 42$ (CH_2CO) was evident. Treatment of authentic VI with Fenton's reagent (hydrogen peroxide and ferrous sulfate) produced a compound with GLC and mass spectral properties identical with those of XI.

The photoproduct X gave strong $M^+ - 28$, $M^+ - 42$, and $M^+ - 70$ ions, indicating an amide and possibly an aromatic

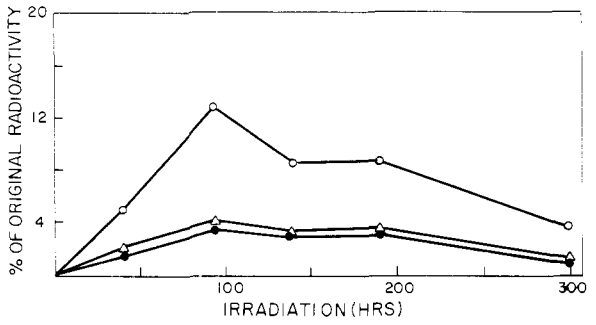


Figure 3. Formation of Sustar photoproducts IV (○), VI (△), and VII (●) at pH 3.6 (FS240 Lamp).

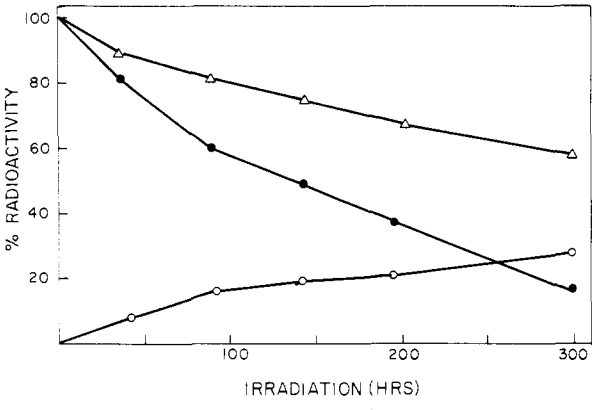


Figure 4. Photodegradation rate of [^{14}C]Sustar (●), formation of polar products (○), and ^{14}C recovery (△) (pH 3.6, FS40 lamp).

aldehyde. No $M^+ - 30$ ion was observed, indicating that X is not the isomeric nitroso compound. When X was treated with acid, it rapidly became colored and would not move on TLC, consistent with acid-catalyzed condensation of aminobenzaldehydes (Horning, 1955). This photoproduct was not formed when Sustar was irradiated under nitrogen, indicating that oxygen is required for its formation.

The mass spectrum of VII showed the characteristic $M^+ - 42$, indicating that the acetamide was intact. Loss of CF_3 gave the $M^+ - 69$ ion, and elimination of HF was observed from the deacylated ion, providing $M^+ - 62$. VII did not react with diazomethane, was extracted from neutral photolysis solutions, and lacked the characteristic $M^+ - 133$ of the sulfonamide. VII also was produced in deaerated solutions; oxygen was not required.

The appearance and loss of the three major photoproducts (IV, VI, and VII) were monitored using [^{14}C]-Sustar (Figure 3), as was the loss of parent and accumulation of chromatographically immobile material (Figure 4). All three peaked in concentration in less than 1 half-life of Sustar, and as usual IV was the major photoproduct. The trap on the exit port of the reactor accounted for less than 0.1% of the initial radioactivity, while aqueous KOH solution did trap quantitatively the radioactivity lost as CO_2. The radioactivity balance was 98% in initial samples, but dropped to 68% at the final sampling when CO_2 was not trapped.

Neutral Photolysis. The photochemical reactivity of Sustar at pH 7.2 in sunlight was rather low (Figure 2). Even with the FS40 lamp, no extractable products accumulated in concentrations greater than 0.5% of the starting concentrations of Sustar. The photoproducts were the same as those from the acidic photolysis except for a minor, unidentified compound (XIII) which was extractable from neutral aqueous solutions and also formed in solutions that had been deoxygenated. Its mass spectrum was similar to that of VII but without the acetyl group, and IR spectra indicated an aromatic amine (3400 and 3550 cm^{-1}) as well as a strong absorption at 1730 cm^{-1} characteristic of a carbonyl. Its small amount precluded final identification.

Table II. Sustar Phytolysis in Creek Water[a]

time, days	Sustar recovery (% of control)[b]	unextractable ^{14}C, %[c]	total ^{14}C recovery (% of control)[d] pH 8.6	pH 2.0
0	103	2	100	98
9	35	35	97	77
17	29	45	92	77

[a] Initial concentration, 2×10^{-6} M. [b] Control recovery 89–92%. [c] Control unextractable, 2%. [d] Control recovery 100–103%.

As before, IV and VII predominated, and V was present in lower concentrations. Small quantities (0.01–0.05%) of the other photoproducts also were present. The irradiations produced colored, polar compounds not present in similar irradiations at pH 3.0, but attempts to separate and identify them were not successful.

Irradiation of [^{14}C]Sustar at neutral pH produced IV and VII near the limit of detection, and they were not quantitated. As before, loss of radioactivity in the photolysate could not be accounted for in a resin trap and presumably is due to generation of carbon dioxide.

Sunlight Irradiation of Sustar in Natural Water. In order to more closely simulate its environmental fate in natural water, [^{14}C]Sustar was exposed to outdoor sunlight in water from a creek adjacent to the University of California, Davis campus. The water was sterilized at 160 °C for 30 min and filtered prior to addition of the Sustar. No photoproducts were detected within 17 days, and the irradiated samples did not differ from the controls except for a major nonevaporative loss of Sustar (Table II). When the extracted aqueous samples were evaporated and the residue subjected to TLC, the radioactivity remained at the origin except for that representing unextracted Sustar. ^{14}C recovery was nearly quantitative from irradiated alkaline solutions and controls, but only 84% of the radioactivity initially in the irradiated solutions could be accounted for after acificiation and solvent extraction, due primarily to release of $^{14}CO_2$.

The failure to observe extractable photoproducts was not unexpected, since the sensitivity of the ^{14}C method was limited to 0.3% of the added Sustar. The pH of the natural water was higher than had previously been used and could result in accelerated loss of IV, which is unstable to base. Since the trifluoromethyl group was not labeled, neither V nor XII could be monitored.

Photochemistry of Sustar in Water. The photoproducts observed in irradiated solutions of Sustar are primarily associated with reactions of the sulfonamido group and only one (IX) was generated from the acetamido group. We propose that they arise through two distinct pathways: sulfonamido radical formation (Figure 5) and anilino radical formation (Figure 6). As shown in Figure 5, oxidation of radical Ic at the para position generated the sulfonimide II which was hydrolyzed to IV and V (Fieser, 1956). This hydrolysis also was evident during the attempted purification of synthesized II.

The photochemical formation of sulfonamido radicals has been demonstrated previously, from *N*-chlorosulfonamides (Ohashi et al., 1970), and appears prominently in the photochemistry of Sustar. Although oxygen conceivably might react directly with the sulfonamide

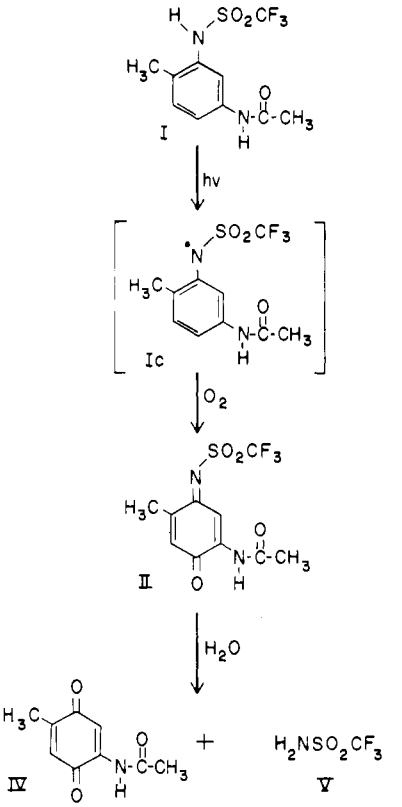


Figure 5. Proposed Sustar photodegradation via the sulfonamido radical (Ic).

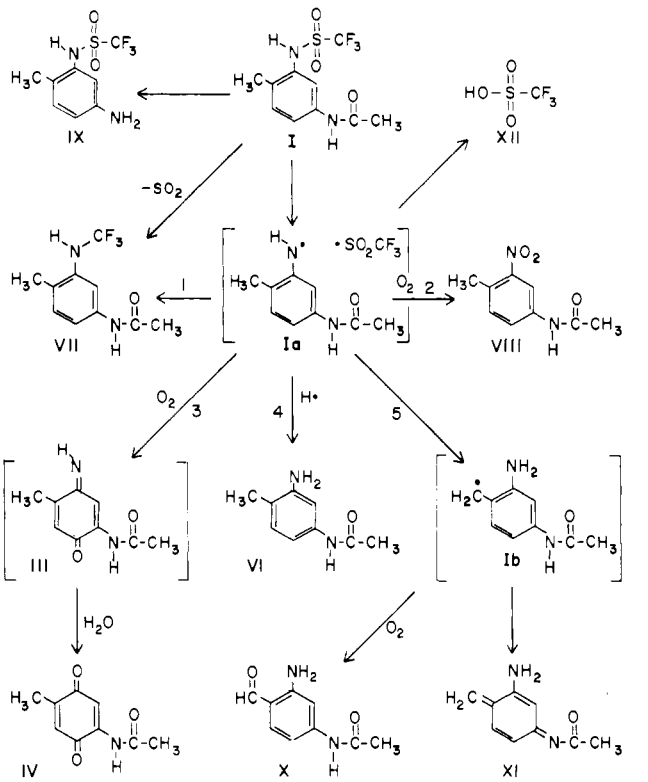


Figure 6. Proposed Sustar photodegradation via the anilino radical (Ia).

radical, Istratoiu et al. (1973) indicated that sulfonanilide radicals protected in the para position do not react with oxygen. The mechanism of ring oxidation to the quinonimide II probably is that suggested for generation of quinonemethides from polystyrene (Achhammer et al., 1953) and benzoquinone from autooxidation of phenol (Scott, 1965).

Figure 6 presents a rationale for photoproducts generated from cleavage of the N–S bond and subsequent reactions of the photochemically generated aniline radical (Ia). Sulfur dioxide extrusion (reaction 1) would provide VII, a major photoproduct observed in all experiments. Elimination of SO_2 with radical recombination is well documented for aromatic sulfones (Block, 1969), the related sultams (Durst and King, 1966), and sulfamides (Nilles and Zabik, 1975).

N-oxidation of the anilino radical (reaction 2) produces the nitro compound VIII. The exact mechanism of this process is not known, although nitro compounds previously have been found after photooxidation of anilines and aniline derivatives. Mansour et al. (1975) found 3,4-dichloroaniline to be photooxidized to 3,4-dichloronitrobenzene on surfaces and in the vapor phase, and Nilles and Zabik (1975) observed nitro formation in photooxidations of bentazon (XIV).

Alternatively, the anilino radical may undergo oxidation on the aromatic ring (reaction 3), as in the oxidation of the sulfonamido radical, to produce a quinoneimine which is spontaneously hydrolyzed in water to the quinone IV (Adams and Reifschneider, 1955). The trifluoromethanesulfonamide group is very stable to hydrolysis, and the formation of VI may be due to intermolecular hydrogen abstraction (reaction 4). This, or intramolecular hydrogen abstraction from the *o*-methyl group (reaction 5), could generate radical Ib which is oxidized to the observed quinoneimide XI or to the aldehyde X; hydrogen abstraction by anilino radicals has been demonstrated in studies on the antioxidant activity of aromatic amines (Scott, 1965). Further oxidation of X to the corresponding acid probably occurs, although it was not detected due to masking by unreacted Sustar.

The photochemical generation of radicals Ia and Ic was evident in Sustar irradiations at both acidic and neutral pH by the formation of V, VI, and VII as major products. Although the same photoproducts were observed at both pH values, the relative amounts of each were different. This result may be due either to a difference in the basic photochemistry or further reactions of the photoproducts; a substantial rate difference was noted between the acid and neutral photolysis, and several unidentified polar products were observed in irradiated neutral or alkaline solutions of Sustar which were not found in acidic ones. Characterization of these colored, chromatographically immobile photoproducts was not attempted, but previous work on aniline herbicide photooxidation (Rosen et al., 1970; Moilanen and Crosby, 1972) has shown extensive formation of polymeric material having characteristics similar to those of humic substances.

Two additional photoproducts (XV and XVI) were present in Sustar solutions irradiated with a medium-pressure mercury arc (>90% 254-nm radiation) but were not found in those irradiated with only the longer wavelengths available in the solar spectrum. They result from a photo-Fries rearrangement (1,3 and 1,5 shifts of the trifluoromethanesulfonyl group), a reaction well-known for *N*-arylamides of carboxylic acids (Bellus, 1971) but reported only once previously with a sulfonanilide (Nozaki et al., 1966). These workers found exclusive para rearrangement while our work indicated the probable presence of both ortho and para rearrangement products.

Environmental Photodecomposition of Sustar. The pH of natural water generally lies between 6 and 9 (Stumm and Morgan, 1970). Consequently, Sustar or its salts would be at least 97% ionized in both the solution in which they are applied and in waters which they might contact.

Although the half-life of a 100 ppm solution of Sustar in dilute phosphate buffer at pH 7.2 was much longer (12 days) than at pH 3.6 (5 days), that of an environmentally more realistic concentration of 0.6 ppm in filtered creek water (pH 8.6) was only about 6 days. The decreased stability in natural water may be due to photosensitization by natural solutes (Lykken, 1972) or photochemically generated oxidants (Draper et al., 1976; Zepp et al., 1977).

The extractable organic photoproducts all had half-lives shorter than that of Sustar and would not be expected to accumulate. The observed terminal products consisted of unextractable, highly polar substances and carbon dioxide which probably formed via ring cleavage of quinones such as IV (Wong and Crosby, 1978). Both trifluoromethanesulfonic acid (XII) and its amide (V) were detected even after extended irradiation and appear to be photochemically stable.

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Photoreactions of Hydroxychlordene in Solution, as Solids, and on the Surface of Leaves

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The photoreactions of the heptachlor transformation product 1-*exo*-hydroxychlordene (*exo*-4,5,6,7,-8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-ol) (**2**) dissolved in organic solvents, as a solid on glass, and dispersed on plant leaf surfaces have been investigated. In addition to the (2 + 2) cycloaddition typical for this substance class, an entirely novel intramolecular photoisomerization reaction was found. This reaction leads to cyclic ketone, 1,1a,2,2,3,*exo*-6-hexachloro-1a,2,3,3a,5a,5b-hexahydro-1,3-methano-1*H*-cyclobuta[*cd*]pentalen-4-one (**8**), whose structure was established by spectral data obtained by mass spectrometry, infrared spectrometry, and ^{1}H and ^{13}C nuclear magnetic resonance measurements.

The degradation of pesticides under both biotic and abiotic conditions leads to residues which can accumulate in the biosphere. In this connection the reactions and changes of pesticides caused by solar UV light are especially important (Crosby et al., 1965; Ivie et al., 1974; Gäb et al., 1975; Parlar and Korte, 1977; Liang and Lichtenstein, 1976). Intramolecular photoisomerizations, whose course is controlled exclusively by the excited state, are among the most important and likely pesticide transformation mechanisms. Neither proton-active compounds nor oxygen species [e.g., $^{3}\Sigma^{-}_{g}$ O_2, $^{1}\Delta_g$ O_2, $O(^{3}P)$, or $O(^{1}D)$] are required for these conversions. Consequently, reactions of this type represent the first possible step in many photochemical conversions if the structural requisites for

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