

with Palouse soil, one notices that only 0.14% of the total picloram adsorbed occurs on the clay fractions, while 5.22% is adsorbed in the case of parathion. Picloram can exist in various structural forms depending on pH and temperature (Cheung and Biggar, 1974). Its low total adsorption in general and, on clay in particular, may be attributed to the fact that most of it is in its anionic form. Previous results show that 99.7% was the anionic form based on  $pK_a$  3.4 and Palouse soil paste of pH 5.9, or 96.9% if the soil surface pH is assumed to be 4.9 due to suspension effects. Interactions with the negatively charged clay surface is highly unfavorable, leaving most of its interaction with the organic matter. Parathion has highly polar  $P^{δ+}-O^{δ-}$  and  $P=S$  bonds, as well as a conjugated ring and a polar  $-NO_2$  group and is strongly adsorbed on the clay surface as well as on the organic matter.

As shown in Table IV and system Ia, the iron oxide surfaces adsorbed 6.07% of the picloram. From structural considerations, the anionic picloram is capable of chelating with metal ions with its pyridinium nitrogen and the carboxyl group forming a five-membered ring. Parathion is adsorbed on iron oxides to a lesser extent.

In systems IIa and IIIa parathion is reacting with different soils where it is adsorbed on both the organic matter and clay fraction. However, the adsorption by organic matter may predominate in many soils when it exceeds 1.0%. Yet, in soils relatively free of organic matter, when significant quantities of clay are present, the adsorption of parathion will still be significant.

A simple flow method has been reported which facilitates the study of reaction rates of pesticides in soil. The relative adsorption constant  $k_o$ , which is independent of the experimental conditions was found useful for comparison of reactions between different pesticides and soils. From the reported energies of activation, a dominance of physical interactions is suggested for the adsorption. The equilibrium adsorption results show that picloram interacts mainly with the organic fraction in soil and parathion with both the O.M. and clay fractions. Possible presence of the chemicals in the interlayer space of sodium montmorillonite has been demonstrated by X-ray analysis.

The proposed procedure, aside from supplying a direct measure of the rate of adsorption important for the understanding of the movement of pesticides in soil, supplies activation parameters and insight into the mechanisms of soil-pesticide interactions.

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## Rates of Transformation of Trifluralin and Parathion Vapors in Air

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The herbicide trifluralin ( $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) and the insecticide parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) were released separately to the atmosphere as emulsifiable concentrate sprays. Their vapors were sampled downwind by high-volume air samplers filled with XAD-4 macroporous resin as the trapping medium. Analysis of the air samples indicated rapid photochemical conversion of trifluralin vapor to a dealkylated product (2,6-dinitro-*N*-propyl- $\alpha,\alpha,\alpha$ -trifluoro-*p*-toluidine) and parathion vapor to paraoxon (*O,O*-diethyl *O-p*-nitrophenyl phosphate). Half-lives for conversion were estimated as 20 min and 2 min for trifluralin and parathion, respectively, under comparable midday summer sunlight conditions. The half-life for trifluralin conversion increased to 193 min when the season changed from summer to fall. Trifluralin was stable in the dark; however, parathion showed some conversion to paraoxon on a summer night (131-min half-life). Results from laboratory experiments conducted under simulated sunlight conditions were consistent with the field results. Rates of photochemical conversion in the laboratory were significantly increased when 1–3 ppm ozone was added to the reaction flask.

While it has long been known that pesticides may enter the atmosphere during and after application, the role of

chemical reactions in the dissipation of airborne pesticide residues has only recently been investigated. For example, chemical conversion takes place when the vapor of aldrin, dieldrin, or DDT is exposed to simulated sunlight (Crosby and Moilanen, 1974; Moilanen and Crosby, 1973), and

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under both laboratory and field irradiation of trifluralin (Soderquist et al., 1975) and parathion vapors (Woodrow et al., 1977). The formation of epoxidized (aldrin), hydroxylated (DDT), dealkylated (trifluralin), and oxon (parathion) products suggested photooxidation as a primary reaction mechanism in irradiated atmospheres. This is not surprising since many pesticides undergo such a reaction on surfaces and in solution (Crosby, 1973).

We were, however, surprised by the rapid rate with which some photooxidations occurred in the air under field conditions. The conversion of parathion to paraoxon, for example, was estimated from analysis of vapors downwind from a treated orchard to occur with a half-life of only 1–10 min (Woodrow et al., 1977). In the present study we have attempted to establish a method for estimating more accurately the rate of photooxidation of pesticide residues in the field atmosphere and to correlate the field results with those obtained under controlled conditions in a laboratory photoreactor. The latter was particularly useful for investigating the role of atmospheric oxidant, such as ozone, in the course and rate of reaction. The test chemicals were the insecticide parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) and the herbicide trifluralin ( $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine).

#### MATERIALS AND METHODS

**Materials.** Parathion 4EC (PaCoast Chemical Co., Sacramento, Calif.), Treflan EC (44.5% trifluralin; Elanco Products Co., Indianapolis, Ind.), and lindane (20% w/w; Cooke Laboratory Products, Pico Rivera, Calif.) were obtained from commercial sources. Analytical standards were obtained from the Environmental Protection Agency, Beltsville, Md. Solvents were distilled twice from commercial grades except for ethylene glycol (EG) which was purified from reagent grade solvent (Mallinckrodt Chemical Works, St. Louis, Mo.) by the procedure of Sherma and Shafik (1975). Amberlite XAD-4 (Rohm and Haas, Philadelphia, Pa.), 20/50 mesh, was cleaned before use by rinsing with 0.02 M hydrochloric acid and water, followed by Soxhlet extraction with acetone.

**Vapor Drift.** Parathion was released to the atmosphere by aircraft 3 m above ground at 4:00 p.m. on June 4, 1976, as an aqueous emulsified suspension of 3.14 kg of parathion in 380 L of water. About 5 min were required to make six passes over an 805-m front during which time high-volume (Hivol) samplers (Microchemical Specialties Company, Berkeley, Calif.), filled with 60 g of XAD-4, were operated (Woodrow et al., 1977). The air sampling was continued for several minutes after release had been terminated. During air sampling, the Hivol samplers were placed at 160 m and 400 m downwind from the spray front and had typical flow rates of 60–90 m<sup>3</sup>/h. Trifluralin was released over a 36–43 m front as a 6-L aqueous emulsified suspension containing 0.95 L of Treflan EC using a backpack mist blower (KWH, Holland) at noon on August 5 and 12 and on October 5, 1976. On the latter date, a mixture of 0.95 L of Treflan and 1.9 L of lindane, used as a stable tracer (Glotfelty et al., 1976), was released. Release of trifluralin required 15–20 min, during which time, and for several minutes after, Hivol air samplers, filled with 30 g of XAD-4, were operated. The air sampling stations were placed downwind of the spray front at distances up to 200 m. The average temperatures, relative humidities, and wind speeds for the three experiments were, respectively, 28 to 30 °C, 20 to 30%, and 1.3 to 3.6 m/s.

**Analysis.** After each field experiment, the samples were packed immediately in dry ice, transferred to the laboratory and stored at –10 °C until analyzed. The XAD-4 air samples were eluted with 100 and 200 mL of ethyl acetate, for 30 and 60 g of XAD-4, respectively, on a rotary shaker for 1 h. The ethyl acetate was then decanted and filtered using additional portions (25 mL) of ethyl acetate to rinse the flasks.

Analysis for parathion and paraoxon (*O,O*-diethyl *O-p*-nitrophenyl phosphate) was carried out by gas chromatography (GLC) using a Varian Model 2100 gas chromatograph equipped with a rubidium sulfate alkali flame ionization detector (AFID) at 210 °C and a 1.8 m × 2 mm (i.d.) glass column containing 10% DC-200 on 100/120 mesh Chromosorb W at 200 °C. Trifluralin, including the sample containing lindane, was analyzed with a Varian Model 1700 gas chromatograph equipped with a tritium foil electron capture (EC) detector at 210 °C and a 1.8 m × 3 mm (o.d.) glass column containing 3% OV-17 on 80/100 mesh Chromosorb G at 180 °C. After analysis for trifluralin, a 50-mL aliquot of the XAD-4 extract was concentrated to 0.5 mL and 20- $\mu$ L aliquots were injected onto a 25 cm × 4 mm (o.d.) Vydac reverse phase column ( $\mu$ C-18) (Applied Science Corp., State College, Pa.) at room temperature. The column was eluted with 70% methanol in water using high-pressure liquid chromatography (LC) and an ultraviolet detector at 254 nm (Laboratory Data Control, Riviera Beach, Fla.). The elution volume for each compound was determined using standards. The fractions suspected to contain trifluralin products I (2,6-dinitro-*N*-propyl- $\alpha,\alpha,\alpha$ -trifluoro-*p*-toluidine) and II (2,6-dinitro- $\alpha,\alpha,\alpha$ -trifluoro-*p*-toluidine) were analyzed using the same gas chromatographic conditions as for trifluralin. Fractions suspected to contain III (2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole) and IV (2-ethyl-7-nitro-5-trifluoromethylbenzimidazole) were analyzed using a Varian Model 2100 gas chromatograph equipped with an AFID at 210 °C and a 1.8 m × 2 mm (i.d.) glass column filled with 3% OV-17 on 80/100 mesh Chromosorb G at 180 °C. Quantitation was done by comparing peak heights with those of standard injections. Field background levels, obtained by sampling air prior to release of the pesticides, were below the limit of detectability of <1 ng/m<sup>3</sup> for all the compounds examined.

Recoveries of trifluralin, its transformation products I–IV, and lindane by 30 g of XAD-4 were in excess of 80% when the compounds were added to air at levels near those expected in the field study. Parathion and paraoxon were also trapped in excess of 80% by 60 g of XAD-4. The compounds were vaporized into the Hivol air sampler intake from a wad of glass wool placed on the filter holder in these evaluations. The 8 in. × 10 in. glass fiber filter was not used. Recoveries of the pesticide residues were determined by measuring the amount of the compound remaining unvaporized from the original deposit and that trapped by XAD-4. Recoveries from XAD-4 of trifluralin, its transformation products, and parathion and paraoxon for 5- $\mu$ g fortifications exceeded 80%.

Trifluralin was stable on XAD-4 during sampling. Parathion, however, exhibited some conversion to paraoxon, but the ratio paraoxon:parathion never exceeded 0.158 in any 1-h laboratory tests using 60 g of the adsorbent.

**Vapor-Phase Photolysis.** Parathion and trifluralin (5–10 mg each) were coated on separate watch glasses and placed in 72-L reaction chambers (Crosby and Moilanen, 1974). The base of each reaction chamber was heated to 65 °C and either dry air or air containing ozone was passed

Table I. Summary of Experimental Data Used in Calculating Rates of Trifluralin and Parathion Transformations in Field Air

compd	distance, m <sup>a</sup>	time, min <sup>b</sup>	air concentration, $\mu\text{g}/\text{m}^3$ <sup>d</sup>		-ln R <sup>c</sup>	date
			parent	product		
trifluralin	50	0.25	50.0	0.395	0.0090	8/5/76
	100	0.50	43.4	0.654	0.0171	
	150	0.75	16.7	0.374	0.0253	
	24.4	0.27	234.4	0.826	0.0040	8/12/76
	100	1.10	21.2	0.168	0.0090	
	200	2.19	0.56	0.013	0.0254	
		85.7	1.39	11.4	0.050	0.0050
					0.0053 <sup>e</sup>	
parathion	161	0.95	1.296	0.226	0.1696	6/4/76
	402	2.38	0.411	0.176	0.3740	
	97.5	3.64	0.577	0.041	0.0729	7/23/75 <sup>f</sup>
	402	15.00	0.282	0.038	0.1326	

<sup>a</sup> Distance downwind from spray front. <sup>b</sup> Transit time for vapor cloud from spray front to sampling station. <sup>c</sup>  $R = [\text{parent (mol)}]/[\text{product (mol)} + \text{parent (mol)}]$ . <sup>d</sup> Average of results from two or three samplers at each station. <sup>e</sup> Computed using the lindane tracer rather than product I. Lindane air concentration was  $9.94 \mu\text{g}/\text{m}^3$ . <sup>f</sup> In the absence of sunlight.

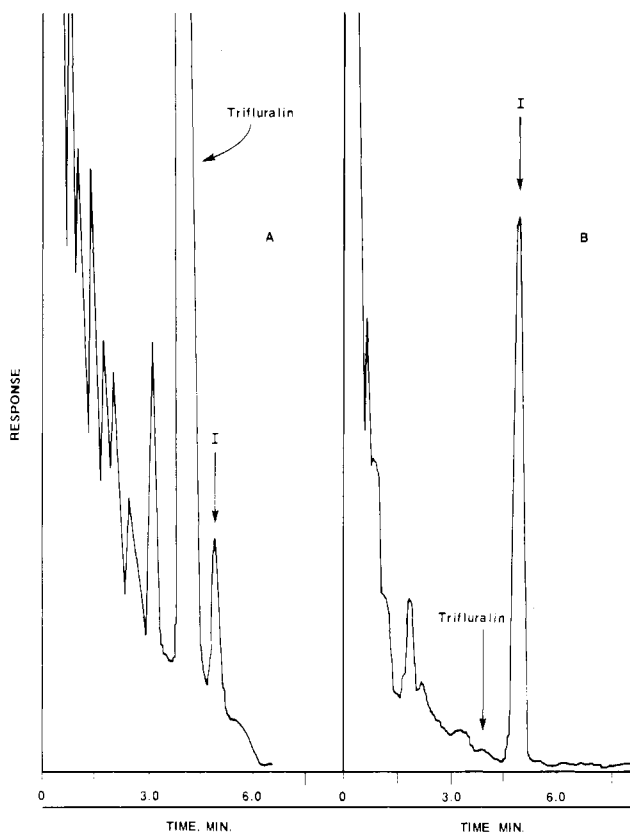


Figure 1. Gas chromatograms of trifluralin product I before (A) and after (B) cleanup by reversed-phase LC.

through at a rate of 200 mL/min for 7 days. The pesticide vapors were irradiated with a collimated beam of light from a Varian Model R 150-7c 150-Watt Xenon arc lamp housed in an aluminum coated parabolic reflector equipped with a Varian Model PS151-1 power source. Ozone (1–3 ppm) was produced by a generator consisting of a quartz Pen Ray lamp along side a quartz flow tube (Ultraviolet Products, Inc., San Gabriel, Calif.). Ozone concentrations were measured in the air entering and exiting the reaction chambers after 24 h of purging at 175 mL/min using an ozone meter (Mast Development Co., Davenport, Iowa) and were found to be essentially identical. The pesticides and their volatile photoproducts were trapped in 130 mL of EG in a gas washing bottle and they were extracted from EG by the procedure of Sherma and Shafik (1975). The experiments were repeated with the lamp off, with and

without ozone, as dark controls.

## RESULTS AND DISCUSSION

**Field Vapor Drift.** The essence of our method for estimating the rate of atmospheric conversions under field conditions consisted of releasing the pesticides as emulsifiable concentrate sprays along a broad front perpendicular to the direction of the prevailing wind, and sampling the resulting airborne residues at varying distances downwind. We assumed that under the field conditions of low relative humidity (20–30%) and high air temperature (28–30 °C) the aqueous spray droplets would quickly evaporate favoring increased pesticide vapor concentration in the atmosphere at the downwind sampling stations. However, it is possible that the pesticides may have been sampled as a mixture of fine aerosols and vapor; our air sampling methodology could not differentiate between the two forms.

Air samples containing trifluralin were fractionated by reversed-phase LC (Kearney et al., 1976) prior to EC–GLC detection to adequately enrich potential breakdown products and to minimize background interference. This led to the detection of a single photoproduct, product I. Gas chromatograms of this compound before and after LC are given in Figure 1. Simultaneous GLC determination of parathion and paraoxon, the only parathion photoproduct detected, was possible without cleanup due to the selectivity of the alkali flame ionization detector employed.

GLC analysis indicated the rapid conversion of trifluralin and parathion to product I and paraoxon, respectively, under the environmental conditions of our study. Half-lives, computed using the first-order expression  $R_t = R_0 e^{-kt}$ , where

$$R = \frac{\text{parent (mol)}}{\text{product (mol)} + \text{parent (mol)}}$$

except for lindane, where

$$R = \frac{\text{trifluralin (mol)}}{\text{lindane (mol)}}$$

(Table I), indicated that dissipation of the residues to below detectable limits occurred in less than a day (Table II). By contrast, residues of the same pesticides in soil and plant tissues may range from several days to years because of their stabilization in plant lipids and soil organic matter (Probst et al., 1967; Joiner and Baetcke, 1973; Stewart et al., 1971). Lindane was included in the trifluralin experiment on October 5, 1976, as a stable tracer.

**Table II. Half-lives and Rate Constants for Trifluralin and Parathion Transformations in Field Air**

compd	half-life, min	rate constant, min <sup>-1</sup>	date
trifluralin	21	0.0325	8/5/76
	63	0.0110	8/12/76
	193	0.0036	10/5/76
	182 <sup>a</sup>	0.0038 <sup>a</sup>	
parathion	5	0.1430	6/4/76
	131 <sup>b</sup>	0.0053 <sup>b</sup>	7/23/75

<sup>a</sup> Computed using the lindane tracer rather than product I.  
<sup>b</sup> In the absence of sunlight.

Its use in this context is predicated on the assumption that it is chemically stable and has the same volatility characteristics as trifluralin. While we did not experimentally test either assumption, the results of Glotfelty et al. (1976) argue for the stability of lindane vapor relative to trifluralin while the very similar vapor pressures of lindane ( $3.2 \times 10^{-5}$  mmHg at 20 °C) and trifluralin ( $1.0 \times 10^{-4}$  mmHg at 25 °C) (Hamaker, 1972) and their close GLC retention times on nonpolar phases indicate a similarity in their volatilities. Given the margin for uncertainty in these assumptions, it is noteworthy that the use of lindane as a tracer led to calculation of a half-life for the dissipation of trifluralin similar to that computed using product I in this single experiment. This suggests that I was the only photoproduct formed in air during the experiment. Dissipation of the transformation products of trifluralin (I) and parathion (paraoxon) was not followed.

Trifluralin and parathion underwent conversion in our field study chiefly by photolysis. This was suggested by the increased residence times for trifluralin in air as the total sunlight energy decreased with the seasonal change from summer to fall. Moreover, it is in agreement with the reactivity of trifluralin in light on surfaces (Wright and Warren, 1965) and in water (Crosby and Leitis, 1973). Parathion, however, showed a measurable conversion to paraoxon at night during an earlier vapor drift experiment (Woodrow et al., 1977) (Table II). It is thus subject to thermochemical oxidation, although at a much slower rate than with light.

When the dissipation of parathion and trifluralin was normalized to sunlight conditions existing at 12:00 noon June 4, 1976, the resulting half-life approximation for each was 2 min and 20 min, respectively. The difference in residence times was no doubt due to a difference in mechanism for photooxidation. The conversion of parathion to paraoxon involves a replacement of sulfur by oxygen. Dealkylation of trifluralin to give product I involves oxidation of an *N*-propyl group after activation by ultraviolet light; in the presence of ozone, attack is directly on the amine nitrogen prior to oxidative removal of an *N*-propyl group (Kolsaker and Teige, 1972).

**Laboratory Vapor-Phase Photolysis.** Several years ago, we designed a reactor which permitted us to study the vapor-phase photochemistry of pesticides with minimal interference from wall-catalyzed reactions (Crosby and Moilanen, 1974). Studies gave excellent qualitative agreement between laboratory and field results with respect to product distribution (Soderquist et al., 1975); however, photolysis rates under field conditions were typically faster than what would have been predicted from laboratory studies. Moreover, some pesticides which were stable in the laboratory photoreactor underwent facile conversion in the field, indicating that the laboratory simulation was not complete. Comparison of laboratory and outdoor air revealed much higher oxidant levels in the field (0.10 to 0.32 ppm) than in the laboratory photoreactor

**Table III. Half-lives for Trifluralin and Parathion Transformations in Air in the Laboratory Photoreactor**

	half-life	
	trifluralin	parathion
light plus ozone	47 min	23 min
light, no ozone	117 min	41 min
ozone, no light	301 h	351 h
dark, no ozone	no reaction	no reaction

(less than 0.01 ppm). Consequently, a concentration of ozone (1–3 ppm) was maintained in the photoreactor to determine whether the presence of this oxidant would result in a better correlation between field and laboratory results.

Table III contrasts the rate data for parathion and trifluralin with and without light and ozone. For both compounds, the photolysis rate was faster when ozone was present. Moreover, both compounds were oxidized by ozone in the dark, although at much slower rates. Since these results compare well with those from our field study (Table II), it is apparent that oxidant is important when considering the atmospheric fate of pesticides and should be included in the photoreactor for adequate laboratory simulation. Dilling et al. (1976) reported the importance of added oxidant in the simulated atmospheric photolysis of a number of chlorinated hydrocarbon solvents. They found that photolysis rates were much faster for many of the compounds when nitric oxide was added to their reaction chamber.

#### CONCLUSIONS

The method for estimating rates of atmospheric conversion of pesticide vapors in the field by analysis for the primary product is satisfactory if only a single product is formed for the duration of the study, having similar vapor characteristics as the parent. This was the case for the two examples studied, as trifluralin and parathion transformations gave the dealkylated product I and paraoxon, respectively, as the only detectable products. The experimental rates nevertheless should be considered as approximate; half-lives were obtained by extrapolation from measurements made early in the course of reactions, replication was less than satisfactory due to limited equipment availability, and a number of variables existed which were not controlled even within single runs.

Sunlight was an important variable, as half-lives for trifluralin conversion increased significantly with a decrease in sunlight intensity during the summer and fall seasons, and the transformation of parathion was much slower after sunset than during the day. The data indicated that parathion was more rapidly degraded than trifluralin when results for both chemicals were adjusted to the same sunlight intensity.

In the laboratory experiments light and ozone were variables. Transformations of trifluralin and parathion vapors in air were most rapid in the presence of both light and ozone, but it appeared that light was the more important of the two variables. Parathion vapor transformation was two–three times more rapid than that for trifluralin when the reactants were exposed to light and ozone, or light only; the same relative trend was noted in the field experiments.

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## Photodecomposition of Sustar in Water

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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-trifluoromethanesulfonyl)-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 [<sup>14</sup>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-acetamido-*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 ( $CDCl_3$ ),  $\delta$  8.2 (s, NH), 7.6 (s, CH),

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