

of the liberated sulfur-derived moiety interfering with the pathway of microsomal electron transport. Peracid oxidation of *N*-methyl-*N*-phosphorothioylcarbamates liberates sulfur and the *N*-methylcarbamate among other products (Fahmy and Fukuto, 1972). Microsomal metabolism of the *N*-benzenesulfenyl-*N*-methylcarbamate examined in the present investigation results in release of the *N*-methylcarbamate, apparently with inhibition of subsequent microsomal oxidations. Possibly the sulfur- or thiophenyl-derived moiety released on oxidation of the *N*-methyl-*N*-phosphorothioylcarbamate or *N*-benzenesulfenyl-*N*-methylcarbamate inhibits subsequent detoxification of the liberated *N*-methylcarbamate, resulting in a greater overall level and persistence of the toxic *N*-methylcarbamate in some insects than in mammals. This hypothesis warrants further investigation.

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## Photochemistry of Bioactive Compounds. Kinetics of Selected *s*-Triazines in Solution

Luis O. Ruzo, Matthew J. Zabik,\* and Robert D. Schuetz

The rate constants (*k*) for several 2-methylthio and 2-halo-4,6-bis(alkylamino)-*s*-triazines have been calculated in methanol, *n*-butyl alcohol, and water solutions. The rate of disappearance of the starting material (I-XII) has been found to be dependent on the nature of the halogen and

alkyl substituents and the solvent employed. A decrease in *k* was observed in the order I-Br-Cl-F and  $-C_2H_5 > -C_3H_7$ . All photoreactions showed zero-order rate constants. The rate constant in methanol was found to be considerably greater than that calculated in *n*-butyl alcohol.

Effects of sunlight and laboratory ultraviolet light on pesticides have been investigated with renewed interest in the past decade (Dilling, 1966). Changes in the ultraviolet spectra of photolyzed solutions of *s*-triazines and a decrease in the phytotoxicity of unidentified photoproduct mixtures have been reported (Comes and Timmons, 1965; Jordan *et al.*, 1963, 1965). Jordan *et al.* (1970) summarized the literature on *s*-triazine photochemistry to that date.

Recent investigations in this laboratory (Pape and Zabik, 1970, 1972) have demonstrated the generality of the photochemical solvolysis of 2-halo and 2-methylthio-*s*-triazines. Irradiation of the former in water, methanol,

and *n*-butyl alcohol solutions resulted in the formation of the corresponding 2-hydroxy and 2-alkoxy derivatives. Photolysis of 2-methylthio-*s*-triazines resulted in photoreduction *via* intramolecular elimination with hydrogen transfer.

The purpose of the present investigation was to extend the knowledge of the photochemistry of symmetrical substituted triazines. The rate variations caused by solvent and substituent effects indicate certain characteristics of the excited state which will be useful in the understanding of their photoreactions.

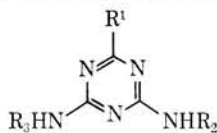
#### MATERIALS AND METHODS

***s*-Triazines.** Authentic samples of I-V and IX-XI were supplied by Geigy Agricultural Chemicals, Ardsley, N. Y. 2-Iodo-*s*-triazines (VI-VIII) were supplied by Z. D.

\*Departments of Chemistry and Entomology, Michigan State University, East Lansing, Michigan 48823.

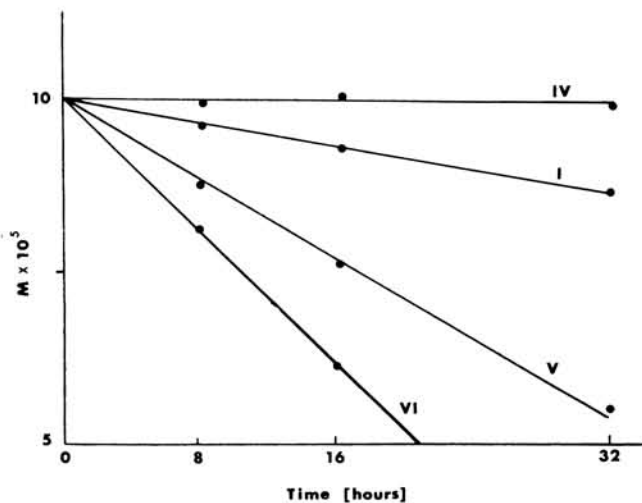
Table I. *s*-Triazines

<i>s</i> -Triazine	Designation	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
Simazine	I	Cl	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
Atrazine	II	Cl	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>
Propazine	III	Cl	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>
Fluorosimazine	IV	F	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
Bromosimazine	V	Br	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
Iodosimazine	VI	I	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
Iodoatrazine	VII	I	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>
Iodopropazine	VIII	I	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>
Simetryne	IX	SCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
Ametryne	X	SCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>
Prometryne	XI	SCH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>

Table II. Rate Constants<sup>a</sup> of *s*-Triazines

<i>s</i> -Triazine	10 <sup>10</sup> <i>k</i> (MeOH)	10 <sup>10</sup> <i>k</i> (BuOH)
Simazine <sup>b</sup>	1.01	0.61
Atrazine	0.69	0.52
Propazine <sup>c</sup>	0.35	0.49
Fluorosimazine	0.20	0.10
Simazine	1.01	0.61
Bromosimazine	3.83	0.79
Iodosimazine	6.61	1.15
Iodosimazine	6.61	1.15
Iodoatrazine	2.43	0.94
Iodopropazine	0.60	0.70
Simetryne	7.40	0.97
Ametryne	2.77	0.83
Prometryne	1.39	0.73

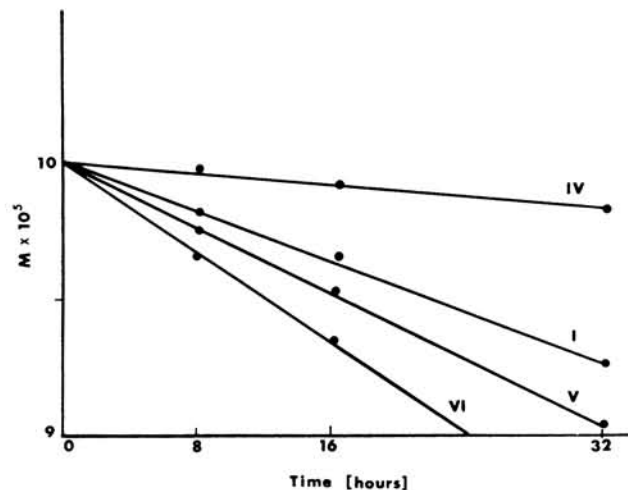
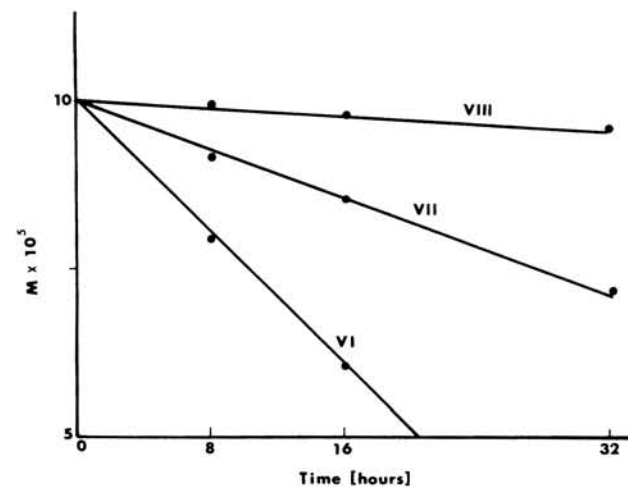
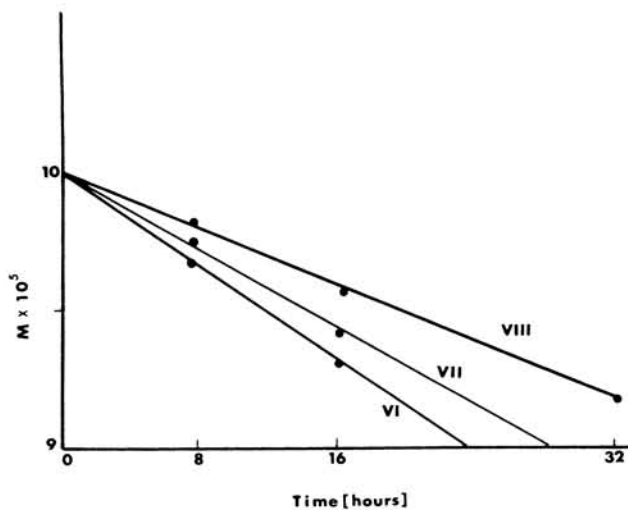
<sup>a</sup>  $kt = A_0 - A$  (mole  $l^{-1}$   $sec^{-1}$ ). <sup>b</sup> In water  $10^{10} k = 0.66$ . <sup>c</sup> In water  $10^{10} k = 0.28$ .

Figure 1. Rates of photolysis of 2-halo-4,6-bis(ethylamino)-*s*-triazines in methanol.

Tadic (Faculty of Technology, Belgrade University, Yugoslavia) (see Table I).

#### CHROMATOGRAPHY

Column and thin-layer chromatographic (tlc) separations of products were accomplished on silicic acid (AR,

Figure 2. Rates of photolysis of 2-halo-4,6-bis(ethylamino)-*s*-triazines in *n*-butyl alcohol.Figure 3. Rates of photolysis of 2-iodo-4,6-bis(alkylamino)-*s*-triazines in methanol.Figure 4. Rates of photolysis of 2-iodo-4,6-bis(alkylamino)-*s*-triazines in *n*-butyl alcohol.

100 mesh) and silica gel, respectively. The chromatographic solvent system was chloroform-acetone (9:1). Glc analyses were performed on a Beckman GC-4 gas chromatograph equipped with a flame ionization detector and a 6-ft stainless steel column, packed with 5% Carbowax 20M on 60-80 mesh Gas Chrom Q (Applied Science Labo-

ratories, State College, Pa.). Column temperatures ranged from 150 to 220° (isothermal conditions) and the carrier gas flow was 40 ml/min (prepurified helium).

**Photoreduction Rates.** Methanol and *n*-butyl alcohol solutions were 10<sup>-4</sup> M. Water solutions were 10<sup>-5</sup> M. Samples, 10 ml each, were placed in borosilicate tubes fitted with Teflon stoppers (volume remained constant throughout the reaction period). Irradiation was carried out for periods of 1-32 hr at 300 nm at 40°. A "merry-go-round" apparatus was used to ensure equal exposure of all samples to uv irradiation. The light source used was a Rayonet reactor equipped with RUL 3000 lamps (maximum output at 300 nm) (The Southern N.E. Ultraviolet Co.).

After irradiation, 2- $\mu$ l aliquots were injected in the gas chromatograph and *s*-triazine disappearance was measured (peak areas were measured by weight). From the amount reacted ( $A_0 - A$ ) and the elapsed time ( $t$ ) the rate constants ( $k$ ) were calculated (Table II).

## RESULTS AND DISCUSSION

As shown in Table II and Figures 1-4, the rate of photoreduction is dependent on at least three factors. The nature of the halogen substituent (Figures 1 and 2) has a definite influence on the rate. The value of  $k$  calculated decreases rapidly in the order I-Br-Cl-F. These results are in agreement with the known dissociation energies of the corresponding carbon-halogen bonds. The large difference between the rates for iodo- and bromo-substituted triazines and those for chloro- and fluoro-substituted ones may also be the result of the increased interaction between the nonbonding electrons on iodine and bromine with the  $\pi$ -system in the ring. Both these halogens are known to undergo valency shell expansion (Forbes, 1959) especially in the excited state. This heavy atom effect facilitates intersystem crossing.

The rate of reaction depends on the nature of the solvent employed as well. A decrease in  $k$  is observed when *n*-butyl alcohol is used instead of methanol or water. The rate of photoreaction in the latter solvents is approximately the same (Table II). This effect is probably the re-

sult of a difference in polarity of the solvents involved and of their viscosity. Polar solvents are known to decrease the energy required for  $\pi-\pi^*$  transitions (Forbes, 1960).

<i>s</i> -Triazine	First absorption band	
	$\lambda$ (methanol)	$\lambda$ (1-butanol)
Simazine	268	262
Atrazine	248	244
Propazine	237	235

*s*-Triazines with ethyl substituents in the 4 and 6 *N* positions show a greater  $k$  value than those with isopropyl groups (Table II, Figures 3 and 4). The main difference in these alkyl groups is their size. As shown above, the increase in chain length results in a decreased wavelength of absorption. Steric effects are known to disturb the geometry of an excited state (Ruzo *et al.*, 1973). This fact may explain our observations; however, further investigation is necessary in order to assess its importance in the case of *s*-triazine photochemistry.

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## Photodecomposition of *p*-Chlorophenoxyacetic Acid

Donald G. Crosby\* and Anthony S. Wong

Aqueous solutions of 4-CPA (*p*-chlorophenoxyacetic acid) decomposed readily under sunlight or laboratory ultraviolet light (300-450 nm) to provide principally *p*-chlorophenol, phenol, hydroquinone, *p*-chlorophenyl formate, phenoxyacetic acid, *p*-hydroxyphenoxyacetic acid, and humic acids. These products represent oxidative remov-

al of the side chain, replacement of the chlorine by hydroxyl or by hydrogen, and polymerization of unstable intermediates. Formation of *p*-chlorobenzonitrile by irradiation of 4-CPA in the presence of cyanide ions substantiated that the corresponding replacement of the ring chlorine by hydroxyl was a photonucleophilic reaction.

The effects of ultraviolet (uv) light on chlorinated phenoxyacetic acids have been reported by several investigators. Kelly and Pinhey (1964) irradiated *p*-chlorophenoxyacetic acid (4-CPA) in ethanol with a medium-

pressure mercury arc lamp and recovered phenol as well as *o*- and *p*-hydroxyphenylacetic acids from the migration of the side chain. Crosby and Tutass (1966) reported that irradiation of 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution with a low-pressure lamp resulted in 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,4-benzenetriol, and humic acid from processes involving mainly the removal of the side

\*Department of Environmental Toxicology, University of California, Davis, California 95616.