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PHOTOCHEMISTRY OF FOUR SYMMETRICAL TRIAZINES

ON CLAY SURFACES

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N'Guessan Adrian Tibebi

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Entomology Pesticide Research Center

ABSTRACT

PHOTOCHEMISTRY OF FOUR SYMMETRICAL TRIAZINES ON CLAY SURFACES

N'Guessan Adrian Tibebi

The photodegradation rate constant and half-life of four s-triazine herbicides at two different concentrations (0.13 and 0.23 μ g/cm²), two pH's (pH₄ and pH_{7.8}) and on three different clay surfaces (montmorillonite, attapulgite and kaolinite) were determined. The rate constants varied from 12.50 sec⁻¹ x 10⁻⁷ (trietazine, 0.23 μ g/cm² on kaolinite at pH_{7.8}) to 63.75 sec⁻¹ x 10⁻⁷ (simetryne, 0.13 μ g/cm² on montmorillonite at pH₄) for the easily extractable fractions of the herbicides.

The rate constants ranged from 0.17 sec⁻¹ x 10⁻⁷ (trietazine, 0.23 μ g/cm² on kaolinite at pH_{7.8}) to 0.63 sec⁻¹ x 10⁻⁷ (simetryne, 0.13 μ g/cm² on montmorillonite at pH₄) for the tightly bound fraction.

The total rate constants were approximately the same as those of the easily extractable portion, ranging from 12.70 sec⁻¹ x 10⁻⁷ (trietazine, 0.23 μ g/cm² on kaolinite at pH_{7.8}) to 64.40 sec⁻¹ x 10⁻⁷ (simetryne, 0.13 μ g/cm² on montmorillonite at pH₄). The rate constants decreased when the concentration of the s-triazines on the clay surfaces reached a certain level. They were faster at pH₄ than at pH_{7.8} and decreased in the order: simetryne > simazine > atrazine > trietazine.

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The half-life times (t 1/2) increased when the pH's of the clays decreased. They were faster on montmorillonite followed by attalpulgite, and kaolinite and decreased in the order: trietazine > atrazine > simazine > simetryne. The mechanism for the variation of the rate constant is discussed from 3 viewpoints:

- The thickness of the herbicide molecular layers on the clay surfaces.
- 2) The effect of molecular structure, and
- 3) The effect on absorption and adsorption of the protonated s-triazine in acidic condition.

There were no significant relationships between extinction coefficient in 295-305 nm wavelength range and the photodegradation rates of the four s-triazines.

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CHAPTER I: INTRODUCTION & HISTORICAL

Triazine herbicides are important means of controlling weeds afflicting man's food crops. It is well understood that with the growing world food crises, triazine herbicides continue to be vital in the production of food and for the protection of man and animals from starvation. The more man's technology develops, the more important it becomes to study its influence on the environment: on the soil (including clays), water, and air, and on the flora and fauna. This is mainly a matter of public concern, questioning whether or not human habitats will not be changed too much by technology to allow healthy and worthwhile living.

The technology for controlling weeds by chemical means instead of by expensive and tiresome mechanical and manual methods is of rather recent origin, especially the sophisticated use of the preventive application of herbicides on the still weed-free clay in the soil. Beneficial as the use of triazine herbicides is, it is not without risk since various types of these chemicals are being introduced into the environment.

Introduction of a herbicide into the ecosystem subjects it to a variety of physico-chemical and biological processes which ultimately determine not only its persistence and fate, but also its degradation products. One of the more important environmental aspects that should

be taken into account is the effect of sunlight. Irradiation by the sun may lead to various photoprocesses and thus to photoproducts which are different from the parent herbicides in their environmental properties and toxicological significance. The photochemical behavior of a triazine herbicide along with its properties must be viewed in light of its overall interaction with elements of the environment such as clay particles as related to behavior, transport and fate.

Knowledge of the dynamics of the photochemistry of triazine herbicides on clay surfaces will lead not only to better understanding of the fate and behavior of chemicals in the clay environment, but will lead to development and improvement in technology for the use of these compounds. It should be mentioned as a factor which influences the various features responsible for safe, efficient, and economical performance of soil applied selective and nonselective herbicides such as: inactivation, positioning and persistence of the herbicide in the soil.

Ultraviolet energy causes the chemical alteration of many pesticides under laboratory conditions (Mitchell, 1961). If such photodecomposition were to occur under field conditions the result(s) might be of major importance in determining the environmental stability and agricultural use of these compounds. Evaluation of such naturally occurring photoproducts and the investigation of their chemistry, photodegradative rate constants, and pharmacology would be necessary to evaluate the merit of their continued use.

Any photochemical reactions in solution or solid adsorbed phases are governed by basic processes divided into two parts that should be understood. The primary photochemical process involves a series of

events that start with the absorption of a quantum of radiation by a molecule and ends with the disappearance of that molecule or its conversion back to its initial ground state or to different excited states. The secondary reactions are those non-chemical processes that lead to chemical products. During the primary processes there are usually a variety of ways for molecular degradation or rearrangement. These paths can include formation of free radicals, ions, intramolecular rearrangements, and other excited molecules which may then react in secondary processes to form new products. The nonchemical primary processes include radiative and nonradiative physical processes which lead to a net chemical change. Therefore, the photochemical reaction of many pesticides involves two operations: (1) absorption of energy leading to excited states and (2) the transformation of the various electronically excited states to chemical products.

The effects of ultraviolet light on herbicides have been investigated by several researchers. Crosby and Tutass (1966) reported that 2,4dichlorophenoxycetic acid (2,4-D) decomposed rapidly in the presence of water and natural sunlight to yield 2,4-dichlorophenol, 4-chlorocatechol, 2-hydroxy-4-chlorophenoxyacetic acid, 1,2,3-benzenetriol, and polymeric humic acids. Rosen and Strusz (1968) found that 3-(pbromophenyl)-1-methoxy-1-methylurea underwent a photolysis reaction when exposed to natural sunlight in aqueous solution. The major product was 3-(p-hydroxy-phenyl)-1-methoxy-1-methylurea.

Changes in the UV spectra of photolysed solutions and decreases in the phytotoxicity of the unidentified product mixture have been reported (Comes and Timmons, 1965; Jordan et al., 1963, 1965). Jordan et al., 1970, summarized the literature prior to 1970 on s-triazine

		N	7)	
		4 N	46	
Substitution on Triazine				
Common	_2		<u> </u>	Designation
Atrazine	C1	NHC2H5	NHiC ₃ H ₇	I
Propazine	C1	NHiC ₃ H ₇	NHIC3H7	II
Simazine	C1	NHC2H5	NHC2H5	III
Trietazine	C1	NHC ₂ H ₅	N(C ₂ H ₅) ₂	IV
Hydroxy-Atrazine	ОН	NHC2H5	NHiC ₃ H ₇	V
Hydroxy-Propazine	OH	NHiC ₃ H ₇	NHiC ₃ H ₇	VI
Hydroxy-Simazine	ОН	NHC2H5	NHC2H5	VII
Hydroxy-Trietazine	ОН	NHC2H5	N(C2H5)2	VIII
Atratone	OCH ₃	NHC2H5	NHiC ₃ H ₇	IX
Promometone	OCH3	NHiC ₃ H ₇	NHiC ₃ H ₇	X
Simetone	OCH3	NHC2H5	NHC2H5	XI
Iodo-Atrazine	I	NHC2H5	NHiC3H7	XII
Iodo-Propazine	Ι	NHiC ₃ H ₇	NHiC3H7	XIII
Iodo-Simazine	Ι	NHC2H5	NHC2H5	XIV
Ametryne	SCH ₃	NHC2H7	NHiC2H7	XV
Prometryne	SCH3	NHIC3H7	NHiC ₃ H ₇	XVI
Simetryne	SCH ₃	NHC2H5	NHC2H5	XVII
	н	NHC2H5	NHC2H5	XVIII
	Н	NHiC3H7	NHC2H5	XIV
	Н	NHiC3 ^H 7	NHiC ₃ H ₇	XX

TABLE I: AUTHENTIC S-TRIAZINES AND PHOTOPRODUCTS

photodecomposition.

Recently, Plimmer and co-workers studied the photolysis of simazine (III) and simetone (XI) at 220 nm in methonal solution by combined glpcmass spectrometry. Simazine (III) yielded XI and other methylated products (Plimmer, personal communication). Plimmer, et al., 1969, also reported the conversion of Simetryne (XVII) to (XVIII) as the result of irradiation of the solid material (Table I).

Pape and Zabik (1970, 1972), in recent investigation have demonstrated the generality of the photochemical solvolysis of 2-chloro-striazines in alcohols, water between 253.7 and 300 nm. Photolysis of I, II, and III in methanol and water yielded XI, X, XI and V, VI, VIII in hydrocarbon, alcoholic, or aqueous solution resulted in the formation of the 4,6-di(alkylamino)-s-triazines XIX, XX and XVIII, respectively (Table I).

In early studies, Jordan et al. (1964) adsorbed simazine [2-chloro-4,6-bis(ethylamino-s-triazine)], atrazine [2-chloro-4-ethylamino-6isoproxylamino-s-triazines] and ametryne [2-methylthio-4-ethylamino-6-isoproxylamino-s-triazine], on filter paper which was then exposed to ultraviolet light and sunlight. The ultraviolet spectrum showed progressive changes indicating the photodecomposition of these striazine herbicides. The photodegradation of the halogenated triazine herbicides involve the replacement of the halogen with the solvent molecule followed by dealkylation reactions as shown by Plimmer and Kingebiel

(1968) and Pape and Zabik (1972a). Apparently the use of 254 nm and 300 nm ultraviolet radiation affects more the reaction rate than the reaction products (Pape and Zabik, 1972a).

The rate of photoreaction is dependent on at least three factors: the first is the nature of halogen substituted as the K 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 and to their ability to undergo valency shell expansion mainly in the excited state. The second is the effect of the N-alkyl substituents. S-triazines with ethyl substituents with the 4 and 6 positions show a greater K value than those with isopropylgroups. This effect is mainly due to differences in size of the alkyl groups as steric effects are known to disturb the geometry of an excited state (Ruzo et al., 1973).

Until now, photolysis in solution was by far the most thoroughly studied process. Unfortunately for environmental photochemists, the substrates of interest are often found as solids or in the absorbed or adsorbed phase; thus it becomes necessary to carry out studies on soil and plant surfaces. It has been shown that the absorption spectrum is shifted when certain compounds are adsorbed on silica gel, for example, trifluralin has a maximum at 375 nm in cyclohexane but at 435 nm on silica gel (Plimmer, 1978). It has been reported that absorption of pesticides on soils decreases their reaction quantum yields (Hautala, 1976). This effect also has been observed where the pesticide interacts with sediment, probably as a result of decreased light availability.

Much speculative attention has been given to the influence of light in the deactivation of s-triazine herbicides on the soil (clay included); but little critical research has been conducted on actual losses from photodecomposition. Nevertheless, sufficient research has been carried out to demonstrate that photodecomposition does occur with some s-triazine herbicides. Usually the silt loam or sandy loam varieties are used as thin film on glass plates. Studies of fluchloralin and bentazon (Nilles and Zabik, 1974) and of pydrin (Holmstead et al., 1978) serve as guide-light.

Gast (1962) reported losses in activity for simazine and atrazine after exposure to ultraviolet (UV) and infrared light radiation, particularly if the herbicides were applied to a dry surface. Dewey (1960) found a decrease in simazine activity after the herbicide was irradiated with a mercury vapor high-pressure lamp. Sheets and Danielson (1961) irradiated simazine on filter paper with UV light, but their results were not conclusive.

Jordan et al. (1965) studied the effect on simazine and atrazine of UV light sources with peak emission of 254, 311, and 360 m μ respectively, representing far, middle, and near UV light. The two herbicides were deposited on aluminum planchets and irradiated for periods up to 400 hours. The absorption of simazine and atrazine under UV is greater at 220 m μ . Following irradiation, absorbance decreased. The greatest decrease occurred after irradiation with 254 m μ and the least with 360 m μ . Loss of simazine and atrazine was rapid during the initial period of irradiation, but as time progressed the rate of loss decreased.

As a continuation of the photochemistry of pesticides in solid phase we examined the photodegradation of four s-triazine herbicides on three different clay surfaces. To fully understand the photochemical behavior of chemicals on clays, it is necessary to know the structures and properties of the clays used and their different power of adsorption at different pHs.

The term clay, refers to the layered aluminosilicate minerals which are considered to be colloidal (less than about one to two μ in diameter). A large number of different types of clay minerals have been found in nature. Each clay mineral has a specific crystalline structure.

All of the layered aluminosilicate clays have a common property: they are made of sheets of tetrahedra of silicon oxide and sheets of octahedra of aluminum oxides and hydroxides. A silicon tetrahedron is formed when the small silica atom is surrounded by four oxygen atoms. An aluminum octahedron is formed when six oxygens or hydroxyls surround a large atom like aluminum. Some clays are made up of alternating sheets of silica tetrahedra and aluminum octahedra. The ratio of tetrahedral sheets to octahedral sheets is 1:1, and these are called the 1:1 clays. Kaolinite is the best known member of this type.

In other clays, the unit layer is made up of two sheets of silica tetrahedra enclosing a sheet of aluminum octahedra. The ratio of tetrahedral sheets to octahedra sheets is 2:1, thus are called 2:1 clays. As unit layers are combined, two tetrahedral sheets lie next to each other. In many cases, the two identical sheets do not attract each other by chemical bonds, but only by relatively week Van der Waals forces, and can be readily separated by water molecules. Such clays

therefore have the ability to swell on wetting and to shrink on drying. Montmorillonite is probably the best of these types.

Sometimes aluminum replaces silicon in the tetrahedral while iron, magnesium, manganese and a few other cations of similar size may replace aluminum in the octahedra. This replacement of ions has been termed "isomorphous substitution". The valance of the replacing cations in many cases is lower than that of the original ions. This means that some of the negative valences of the oxygen atoms are not satisfied internally and this creates an overall net negative charge on the clay surface. This total negative charge has to be neutralized by cations, thus cations such as sodium, potassium, calcium, and hydrogen are attracted to the clay surfaces. These ions may be replaced by other cations in the soil environment and are known as "exchangeable cations", and the amount of exchangeable cations that a clay can retain is known as the clay's "cation exchange capacity" or CEC.

In the 1:1 clays, exchangeable cations are adsorbed only on the exterior surfaces, but in 2:1 clays the cations may also be adsorbed on the interior surfaces. For some of the 2:1 clays, potassium atoms are located between the neighboring tetrahedral sheets and hold the sheets tightly together with electrostatic bonds. Consequently these clays do not shrink or swell and are termed the "nonexpanding" 2:1 clays. Attapulgite illustrates that type of clay. Expanding 2:1 clays have a much greater specific surface area and C.E.C. than the nonexpanding 2:1 clays. Some of the characteristics of selected clay minerals are given in Table II. The expanding 2:1 clays, because of their

greater surface area and CEC, adsorb the triazines to a greater extent, followed by 2:1 nonexpanding and finally 1:1 clays. The degree of association and dissociation is determined by the pH.

CHARACTERISTICS	MONTMORILLONITE	VERICULITE	ATTAPULGITE	KAOLINITE
Type of layering	2:1	2:1	2:1	1:1
Type of swelling	Expanding	Limited Expanding	Non- Expanding	Non- Expanding
CEC (meg./g.)	80-150	120-200	10-40	2-10
<pre>Specific surface (sq. m./g.)</pre>	700-750	500-700	75-25	25-50

Table II: CHARACTERISTICS OF SOME COMMON CLAY MINERALS

Bailey et al. (1968) found that regardless of the chemical character of the adsorbate, adsorption occurred to the greatest extent on the highly acid hydrogen montmorillonite $(pH_{6.8})$. The same author concludes that the magnitude of adsorption of organic compounds with widely different chemical characters is governed by three factors: (1) pH of the clay systems, (2) water solubility, and (3) the dissociation constant of the adsorbate. In this research, our attention was focused on the pH's because the s-triazines undergo acid-base reactions as a function of pH. These workers also found that the adsorption of acidic type compounds was dependent upon the pH of the suspension. For weekly basic herbicides like the s-triazines, surface activity is probably the most important property of the soil or colloid system in determining the extent and the nature of adsorption and desorption. Infrared studies reported by Russel et al. (1968b), Cruz et al. (1968), and Bailey et al. (1970) clearly show that various s-triazines are protonated on montmorillonite surfaces in the presence of a variety of different cations. Weber (1966) in an adsorption study of 13 related s-triazines by montmorillonite found that the maximum adsorption of all the compounds occurred at a pH in the vicinity of the dissociation constant of each compound. A further lowering of the pH resulted in some desorption of each of the adsorbed triazines. He attributed this to the competition of hydrogen ions for exchange sites at low pH levels. This result is directly opposite of that found by Frissel and Bolt (1962) for the adsorption of chloro-s-triazines. They found that about three to four pH units above the dissociation constant, adsorption started to increase as pH decreases down to pH one.

Nearpass (1967), studying the effect of the predominant cation on the adsorption of simazine and atrazine by soils, found that the adsorption of simazine and atrazine is governed largely by the hydrogen ion activity relationship which occurred between the solution and the solid phase of the soil. At equal concentrations atrazine was less strongly adsorbed than simazine.

Frissel (1961) studied the effect of suspension pH and electrolyte concentration on the adsorption of 14 organic compounds, including the chloro-s-triazines (simazine, chlorazine, and trietazine) on the clay minerals illite, montmorillonite and kaolinite. He found that the adsorption process was pH dependent and postulated that the triazines were adsorbed as neutral molecules in neutral and basic environments and as positively charged ions in acidic solutions. Montmorillonite

adsorbed greater amounts of the triazines than illite, attapulgite and kaolinite, respectively.

Harris and Warren (1964) studied the adsorption from aqueous solution of several herbicides, including atrazine and simazine, by bentonite clay. Adsorption of atrazine by bentonite was much greater at $pH_{4.1}$ than $pH_{8.2}$. The higher adsorption at low pH was attributed to the triazines molecule with protons on the clay surface as suggested by Frissel. Simazine was adsorbed in greater amount than atrazine by bentonite at $pH_{8.5}$.

The adsorption from aqueous solution (pH₇ saturated calcium hydroxide) of five s-triazines on 25 soil types, four clay minerals, was determined by Talbert and Fletchall (1965). In almost all cases, adsorption decreased in the order: prometryne > prometone > atrazine > propazine.

Adsorption from aqueous solutions of the 13 triazines by Namontmorillonite clay showed that adsorption was dependent upon the molecular structure of the compound and the pH of the system (Weber, 1966). The key to the amount of adsorption was the molecular structure of the compounds. Decreased adsorption resulted as the 2-substituent was changed in the following order: $-SCH_3 > 0CH_3 > -OH > -C1$.

The purpose of the present investigation was to extend the knowledge of the photochemistry of symmetrical substituted triazines on solid surfaces. In this study the solid phases used were montmorillonite, attapulgite, and kaolinite. The specific objectives were to:

 Develop a comparative study of the photodegradative rate constant of each triazine herbicide in relationship with concentrations, pH's, and clay type.

- Use the rate constants to calculate the half-life time (t 1/2) for the various triazines.
- 3) Establish if possible, relationship between the photodegradative rate constants and the absorbance of the four s-triazines.

CHAPTER II: EXPERIMENTAL

Equipment and reagents

<u>Chemicals</u>: All the s-triazines were analytical standards, obtained from Geigy Agricultural Chemicals, Division of Geigy Chemical Co., Saw Hill River Road, N.Y. and used without further purification. The purities were greater than 98%.

<u>Clay samples</u>: The clay samples were Kaolinite and Attapulgite respectively from Macon Attapulgus, Georgia and Montmorrillonite from Rockville, Mississippi.

<u>Solvent</u>: Methanol used in photochemical reactions was glass distilled. (Burdick and Jackson Laboratories, Inc.; Muskegon, MI).

<u>Photochemical equipment</u>: The photodegradative experiments were carried out in a Rayonet Photochemical Reactor (The Southern N.E. Ultraviolet Co., Middletown, Conn.) fitted with RUL 3000 lamp having peak energy output at 300 nm.

<u>Glass reaction plates</u>: Glass plates were obtained from the Division of American Hospital Supply Corporation. The size of plate was 6.0 x 2.5 cm. (Model Number M6130).

Clay Type	Kaol inite	Attapulgite	Montmorillonite
Structure	(0H) ₈ Si ₄ Al ₄ 0 ₁₀	(он ₂) ₄ (он) ₂ мд ₅ si ₄ н ₂ о	(OH) ₄ Si ₈ (A1 _{3.34} Mg _{.66})0 ₂₀
CEC* (meg/100 g)	3-15	20-30	80-150
Surface area ((M ² /g)	7-30	75-125	600-800
Elements			
\$10 ₂	45.20	55.03	50.20
A1203	37.02	10.24	16.19
Fe ₂ 03	0.27	3.53	4.13
Fe0	0.06		
MgO	0.47	10.49	4.12
CaO	0.52	-	2.18
K20	0.49	0.47	0.16
Na ₂ 0	0.36		0.17
T102	1.26		0.20
H ₂ 0-	1.55	9.73	15.58
Ŀ	12 97	10.13	7.57
H ₂ 0+	13.61		

-4 1 ļ F -CI AV MINEDALS

pH Meter and establishment of pH_4 and $pH_{7.8}$: An Altex 70 pH meter Beckman Instruments, fitted with on Altex combination pH Electrode 531822 was used to measure pH. To obtain clay at pH_4 , 1.25 N HCl was added to different clay slurries while 1 N NOH was used in the same way to obtain a $pH_{7.8}$.

<u>Analytical equipment</u>: GC analyses were performed on a Tracor 560 chromotograph equipped with NP detector. Ultraviolet and visible spectra adsorption determination were performed on a Gilford UV-Vis 2600 spectophotometer interfaced to an HP 7225A Plotter (Hewlett-Packard Corp.) and a PDP-11/40 RSTS/E Computer System (Digital Equipment Corp.).

Experimental procedures

<u>Preparation of clay thin-layer chromatography (TLC)</u>: Each clay was ground, using Arthur H. Thomas Co. Scientific Apparatus, Philadelphia, PA., and a mesh of 106 μ m opening or 0.0041 inch from USA-Standard Testing Sieve Soiltest, Inc., 2205 Lee Streer Evanston, Ill. 60202 to obtain uniform clay which would adhere to the glass plates.

A solution of 3 N sodium chloride (3 N NaCl) was used to obtain the Na-Saturated clay. The different clay solutions were then washed with distilled water to remove excess sodium chloride and with methanol which was the solvent used for the pesticide solution. The clays were dried in a vaccuum oven at 49°C to remove the solvent. A slurry in distilled water was made and pH_4 and $pH_{7.8}$ were established. The overall solutions were dried in the oven at 110°C overnight. Again

the grinder and mesh of 106 μ m opening were used to make thin particles. After that stage aqueous slurries were prepared in distilled water and .75 mm thick layer was spread using TLC apparatus.

The clay TLC plates were stored in an oven at 110°C overnight and then in the drawers in the dark until they were applied. It is important to mention that due to the expansion of montmorillonite, it was very difficult to obtain uniform plates comparable to the kaolinite and attapulgite.

Pesticide application and extraction: Four pesticides belonging to the s-triazine group were then chosen for photochemical investigation. S-triazine solutions, containing 2 and 3.5 μ g were placed on the clay glass slide plates by 1 ml pipette, so that the surface concentration would be 0.133 and 0.233 μ g per cm² respectively, after solvent evaporation. A small amount of solvent was added to each clay TLC plate to cover the surface uniformly when 1 ml of s-traizine solution was not sufficient to cover the whole plate. After the solvent evaporated, a glass cover plate was added and the edges taped to minimize pesticide evaporation. The plates were placed in the photochemical reactor for 4, 8, 12, 24, and 48 hr. periods and were irradiated perpendicular to the light tubes. The irradiation chamber temperature was 34°C-36°C. Each treatment was associated with a dark control. After irradiation, the plates were washed with 5 ml of methanol into scintillation vials for the easily extractable fraction. Anhydrous sodium sulfate was added to dry the methanol solution and a rotavapor was used to reduce the volume to 0.1 ml which was used in the final quantitation. One ul was injected into the Tracor 560-GC.

The bound fraction of the pesticides was obtained by treatment of the plates with ammonium acetate (NH_4oAc) followed by extraction twice with 5 ml methylene chloride (CH_2Cl_2). This fraction was again dried with anhydrous sodium sulfate. The total volume was reduced to dryness and then made up to a (1) ml volume with (CH_3OH) for injection into the Tracor 560 GC.

To compensate for a small amount of pesticide disappearance by evaporation, identically prepared plates were placed in the same photoreactor the top of which was covered by a dark colored wool cloth to prevent exposure to room light, but still allow air flow past the plates. A heating mantle was used to maintain the temperature within the range of 34°C-36°C for these dark controls. The amount of pesticide remaining on the plates, bound or nonbound to the clay samples was quantitated by GC. The values obtained from the irradiated plates were corrected relative to the amount of pesticide which had disappeared from evaporation and/or reactions as shown by the dark controls.

The photodegradative rate constants (K) were determined by least squares analysis (for both the bound and easily extractable fractions and then for the total.) of log (amount pesticides remaining) vs. irradiation time plots. The half-time (t 1/2) were calculated from (K) using the following standard equation: t $1/2 = \frac{0.693}{K}$

For the purpose of estimating the relationship between the photodegradative rate and the absorbance, the maximum absorbance for each pesticide was measured between 295-305 nm and the extenction coefficient was calculated.

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Study of % recovery:
% recovery = Amount of pesticides obtained
X 100
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Three (3) ml of 3.5 ppm solution of the s-triazines was added to 10 g of each clay sample to obtain a concentration of 1.05 (\cong 1 ppm). The solutions were shaken and kept overnight to allow the adsorption of the herbicides and the evaporation of the methanol used as the solvent.

The next morning, the whole samples were treated twice with 40 ml of 3 N ammonium acetate, followed by extraction three times with 30 ml of methylene chloride. The total volume was reduced to dryness and then made up to 1 ml volume with methanol. One μ l of the solution was injected into the Tracor 560 GC. By the comparison to the standard curves the results in Table IV were obtained. These results were used to show how good the standards recovered from the different clays and not as correction factors.

TABLE IV: <u>RECOVERY OF FOUR TRIAZINES FROM THREE DIFFERENT CLAY MINERALS</u> AT pH₄ and pH_{7.8}

	Average % Recovery		
s-Triazines	Ph7.8	рН ₄	Сlaу Туре
Atrazine	82	99	IITE
Simazine	89	96	ILLON
Simetryne	86	75	MORI
Trietazine	89	82	LNOW
Atrazine	93	86	
Simazine	98	86	-GITE
Simetryne	79	82	LAPUL
Trietazine	86	75	ATT
Atrazine	89	96	
Simazine	93	98	4I TE
Simetryne	93	96	AOL IN
Trietazine	82	71	マ

CHAPTER III: RESULTS AND DISCUSSION

Effect of Molecular Structure and Functional Group of s-triazines on Photodegradation Rates

The photodegradation results of four s-triazine herbicides at concentrations (0.13 and 0.23 μ g/cm²) showed that plots of log (amount pesticide remaining) versus time of irradiation where linear, indicating first-order reaction kinetics (Figures 1-12). There were not large differences in the photodegradation rates among the four herbicides, varying from 12.50 to $10^{-7}~\text{sec}^{-1}$ (trietazine, 0.23 $_\mu\text{g/cm}^2$ on kaolinite at $pH_{7.8}$) to 63.80 x 10⁻⁷ sec⁻¹ (simetryne, 0.13 µg/cm² on montmorillonite at pH_4 (Tables XI, XII). For different groups of herbicides, differences due to functional group with substituents in the 2-position and ethyl substituents in the 4- and 6-N positions (simetryne) showed greater K value, and decreased in the order: $R_1 = R_2 = C_2 H_5$ and $R_3 =$ SCH_3 (simetryne) > $R_1 = R_2 = C_2H_5$ and $R_3 = C1$ (simazine) > $R_1 = C_2H_5$, $R_2 = i-C_3H_7$, and $R_3 = C1$ (atrazine) > $R_1 = C_2H_5$, $R_2 = (C_2H_5)_2$ and $R_3 =$ Cl (trietazine). This is true for the easily extractable fraction, the tightly bound, and the total amount of s-triazines at different pH's. This sequence is in good agreement with the solution photodegradation results of Ruzo, et al. (1973), and Zong, et al. (1983). The greater K value with ethyl substituents in the 4 and 6 positions than those with isopropyl groups was mainly due to differences in size of the alkyl

groups as steric effects are known to disturb the geometry of an excited state (Ruzo, et al., 1973).

Influence of Concentration on the Photodegradation

Two different concentrations were irradiated for each s-triazine. Plots of log (herbicide disappearance concentration) versus time, were linear but had different slopes depending on initial concentration. Tables VI and VII of the total photodegradation rates for the four striazines on thin film glass plates of the different clay samples at PH_4 and $PH_{7.8}$ showed that the higher the concentration, the slower the photodegradation rate constants. The apparent decrease in rate constant is probably due to the fact that at higher concentration the herbicides were distributed in thicker layers on the clay surfaces, with the upper layers playing a protective role over the lower layers. Thus, the overall degradation rates decrease as the concentration increases. This is in good agreement with the result of Zong, et al. (1983).

The estimation of molecular size by means of the stereomodel methods indicates that the molecular size of the various pesticides varies between 6.3 - 16.0 Å x 6.0 - 7.5 Å, with the thickness varying between 1.5 Å to 2.5 Å. The calculation using the above value indicates that the number of molecular layers on the clay surfaces in the 0.13 μ g/cm² was approximately 7. There were about 12 layer in the .23 μ g/cm² treatment. J. A. Kitchener (1946) estimated that about 98% of the radiation, of wavelength less than the absorption threshold, which enters a typical crystal may be absorbed within a distance of 10⁻⁶ cm. If we assume that every molecular layer is 2 Å in thickness, then the molecular layer for the .13, and .23 μ g/cm² would be 14 and 24 Å respectively,
that shows the molecular layer of pesticides in high concentration is thicker to permit radiation to penetrate into the layer, so photodegradation is only in the upper herbicides layers. Consequently, the rate constants decreased.

Photodegradation Rates as Influenced by Clays at pH_4 and $pH_{7.8}$

The photodegradation rates of the easily extractable (non-bound) fractions were faster at pH_4 than at $pH_{7,8}$ and decreased in the order: montmorillonite > attapulgite > kaslinite. At pH_4 there is protonation of the s-triazines on clay surfaces, Russel, et al. (1968b); Cruz, et al., (1968); Bailey, et al., (1970); and Frissel and Bolt (1968). The effect of the protonation leads to a complex formation, changing the structure regardless of the type of of the s-triazines and become s-triazine. This complex seems to adsorb more UV light than s-triazine adsorbed in neutral or basic conditions (i.e. on clays at $pH_{7,8}$). If so, the rate constants at pH_4 should be faster than those at $pH_{7,8}$. This assumption was verified by the following supplementary experiment: we determined the UV spectra of 2 ppm solutions of simazine at pH_4 and pH_{7-8} . The absorbance and thus the extention coefficients was higher at pH_4 than at $pH_{7.8}$ (Figures 17 & 18). Therefore, at pH_4 the complex absorbs more than at pH_{7-8} . Consequently, the photodegradation rates were higher.

As for the tightly bound fractions (bound fractions) the photodegradation rates did not fluctuate much. At pH_4 and $pH_{7.8}$ they differed by .01 to .02 sec⁻¹ x 10⁻⁷, varying from .17 sec⁻¹ x 10⁻⁷ (trietazine, on kaolinite) to .625 sec⁻¹ x 10⁻⁷ (simetryne on the same kaolinite). This was due to the fact that little reaction took place, illustrated by low photodegradation rates.

The total photodegradation rate constants for the easily extractable fraction and the tightly ones, were approximately the same as the nonbound portion. Once again, most of the reactions took place with the loosely bound fraction.

Relationship Between the Photodegradation Rate and the UV Absorbance of the Four-Triazines

The maximum energy output of the irradiation source was 300 nm and environmental photodegradation occurs at wavelengths above 290 nm. Since the earth's ozone layer absorbs most of the sun's electromagnetic radiation below that wavelength, we have: estimated the maximum absorbance of the test compounds in 210-340 nm and 295-305 nm regions. At 94 x 10^{-6} M and 93 x 10^{-6} M simetryne and atrazine did not give a measurable absorption. There was no significant relationship between the extinction coefficients and the rate constants of the triazines (Table IX).

s-Triazine	Extraction Solvent	Instrument Detector ¹	Column Packing ²	Column, OC ³	Retention Time, min
Trietazine	Methano]	NP	A	200	2.00
Atrazine	Methanol	NP	Α	200	1.90
Simazine	Methano1	NP	А	200	1.90
Simetryne	Methanol	NP	Α	200	2.90

TABLE V: TRIAZINES ANALYSIS PARAMETERS

¹NP = Nitrogen-Phosphorus detector

 $^{2}A = 6' \times 2 \text{ mm}$ i.d. glass containing 3% silicone SE 30 on 80/100 chromosorb $_{W-HP}$

 $^3 For \ \text{GC-NP}$ detector and injector temperature were 250°C

		Rate	Constant	t (sec ⁻¹ x	10 ⁻⁷)		
s-Triazines	0.	13 µg/c	:m ²	0.	23 µg/c	.m ²	Сlaу Туре
Trietazine	17.75 ¹	.223 ²	17.90 ³	13.05 ¹	.193 ²	14.60 ³	NITE
Atrazine	38.07	.326	38.47	31.08	.215	31.50	ILLO
Simazine	40.50	.441	40.95	33.70	.34	34.10	TMOR
Simetryne	58.16	.602	59.00	53.20	.556	53.80	NOW
Trietazine	16.21	.218	16.50	12.70	.185	12.90	ш
Atrazine	37.75	.2741	37.98	31.01	.207	31.30	LGIT
Simazine	39.50	.442	39.95	32.20	.238	32.60	TAPU
Simetryne	57.01	.601	58.01	52.79	.545	52.98	AT
Trietazine	16.01	.198	16.39	12.50	.174	12.70	
Atrazine	35.49	.253	35.70	30.33	.204	30.65	ITE
Simazine	39.50	.430	39.96	32.10	.336	32.50	NI TO
Simetryne	56.60	.601	57.20	52.44	.543	52.90	KA

TABLE VI:	TOTAL	PHOTODEGRADATION	RATE	CONSTANTS	FOR	FOUR	TRIAZINES	
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ON CLAY SURFACES AT $pH_{7.8}$ OF (1.3 and 0.23 μ g/cm²) HERBICIDES

¹Easily extractable fraction

²Tightly bound fraction

 3 Total amount of 1 and 2

TABLE VII: TOTAL PHOTODEGRADATION RATE CONSTANTS ON CLAY SURFACES FOR FOUR TRIAZINES AT pH_4 OF (0.13 and 0.23 μ g/cm²) HERBICIDES

		Rat	e Constant	c (sec ⁻¹ x	10 ⁻⁷)		
s-Triazine	0.	13 µg/0	cm ²	0.	23 µg/c	m ²	Сlау Туре
Trietazine	19.01 ¹	.23 ²	19.20 ³	14.50 ¹	.198 ²	15.05 ³	VITE
Atrazine	40.37	.401	40.82	33.05	.240	33.08	ILLON
Simazine	42.97	.403	42.06	35.01	.345	35.40	TMOR
Simetryne	63.75	.625	64.40	55.44	.563	55.99	NOM
Trietazine	18.50	.224	18.72	14.01	.185	14.20	ш
Atrazine	39.50	.402	39.91	32.80	.2399	33.11	LGIT
Simazine	39.85	.386	39.99	34.85	.343	35.90	TAPUI
Simetryne	63.50	.607	64.11	54.05	5674	54.66	AT
Trietazine	18.10	.222	18.30	13.78	.179	13.89	
Atrazine	39.40	.343	39.74	32.73	.238	32.97	ITE
Simazine	39.90	.355	40.30	34.70	.340	35.06	DL IN
Simetryne	63.01	.615	63.78	53.60	.5520	54.16	KAI

¹Easily extractable fraction

 2 Tightly bound fraction

 3 Total amount of 1 and 2

TABLE VIII: TOTAL PHOTODEGRADATION HALF-LIFE FOR FOUR TRIAZINES ON CLAY SURFACES AT $pH_{7.8}$ AND pH_4 AND AT PLATE CONCENTRATION OF .13 μ g/cm²

	Half-L	ife, hr	
s-Triazines	^{pH} 7.8	^{рН} 4	Clay Types
Atrazine	50	47	IITE
Simazine	47	45	LILLON
Simetryne	33	30	TMOR
Trietazine	107	100	LNOM
Atrazine	51	48	ш
Simazine	48	48	LGIT
Simetryne	33	30	TAPU
Trietazine	117	103	AT
Atrazine	54	48	
Simazine	48	48	NITE
Simetryne	34	30	AOLI
Trietazine	117	105	\checkmark

TABLE IX: THE ABSORBANCE AND EXTINCTION COEFFICIENT VALUES FOR FOUR TRIAZINES IN MEOH

	Concentration	Absorbance Wavelength	Maximum	E Max	Maximum Absorbance	E Max L/mole cm
s-Triazine	10 ⁻⁰ M	E	Absorbance	L/Mole cm	(295-305 nm)	(395-305 nm)
Simetryne	94	248.0	1.90	20213	0	0
Simazine	66	247.5	1.88	18990	.023	232
Atrazine	93	247.5	1.83	19677	0	0
Trietazine	87	247.5	1.90	21839	.004	46

Figure 1: Total Photolysis of thin film glass plate of montmorillomite $pH_{7.8}$ of (.23 μ g/cm²) s-triazines.

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Figure 2: Total Photolysis of thin film glass plate of attapulgite $pH_{7.8}$ of (.23 μ g/cm²) s-triazines.

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Figure 3: Total Photolysis of thin film glass plate of kaolinite $pH_{7.8}^{-}$ of (.23 μ g/cm²) s-triazines.



Figure 4: Total Photolysis of thin film glass plate of montmorillonite pH_4 of (.25 μ g/cm²) s-triazines.



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Figure 5: Total Photolysis of thin film glass plate of kaolinite pH_4 of (.23 μ g/cm²) s-triazines.

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Figure 6: Total Photolysis of thin film glass plate of attapulgite pH_4 of (.23 μ g/cm²) s-triazines.



Figure 7: Total Photolysis of thin film glass of montmorillonite $pH_{7.8}$ of (.13 μ g/cm²) s-triazines.



Figure 8: Total Photolysis on thin film glass plate of kaolinite $pH_{7.8}$ of (.13 μ g/cm²) s-triazines.

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Figure 9: Total Photolysis of thin film glass plate of attapulgite $pH_{7.8}$ of (.13 µg/cm²) s-triazines.

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QC. QZHZHDIMA HZCOID FDHOH

Figure 10: Total Photolysis of thin film glass plate of montmorillonite pH_4 of (.13 μ g/cm²) s-triazines.

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Figure 11: Total Photolysis of thin film glass plate of attapulgite pH_4 of (.13 μ g/cm²) s-triazines.

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Figure 12: Total Photolysis of thin film glass plate of kaolinite pH_4 of (.13 μ g/cm²) s-triazines.

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Figure 13: UV absorption of 20 ppm simetryne in MEOH.



Figure 14: UV absorption of 20 ppm atrazine in MEOH.

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Figure 15: UV absorption of 20 ppm simazine in MEOH.


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Figure 16: UV absorption of 20 ppm trietazine in MEOH.



FIC 16 . UV ABSORPTION OF 20 PPM TRIETAZINE IN MECH

61 ≺ כס אינס אינס אינס א Figure 18: UV absorption of 2 ppm simazine in MEOH at pH4.



Figure 17: UV absorption Of 2 ppm simazine in MEOH at pH7.8



CHAPTER IV: CONCLUSIONS

The photochemistry of s-triazines on adsorbing thin film glass plates of clays, is a relatively new area of study, but it holds great significance for safety, application, and residue analysis as weel as for advances in fundamental photochemistry.

This study leads us to conclusive results, such as: (1) the effect of functional group with substituents in the 2-position and ethyl substituents in the 4- and 6- N positions on the photodegradative rates, simetryne showing greater K values, and decreased in the order: simetryne > simazine > atrazine > trietazine, (2) the effect of initial concentration on the rate constants due to the distribution of the herbicides in thicker layers on clay surfaces at higher concentration, the upper layers playing a protective role over the lower layers, (3) the effect of protonation of s-triazines in acid condition leading to the formation of the half-life times of the four triazines on clay surfaces at different pHs (5) the lack of consistent relationship between the photodegradation rates and the extinction coefficient.

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