THE THERMAL DEGRADATION CHARACTERISTICS OF ENVIRONMENTALLY SENSITIVE PESTICIDE PRODUCTS

by

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing of research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities.

This publication provides the results of theoretical and laboratory-scale research which examined thermal breakdown behavior of a variety of pesticides and one pesticide container material when subjected to heat such as during open-burning and/or intermediate conditions within an incinerator. The report contains information important to the technical community concerned with excess or waste pesticide disposal via burning or incineration.

E. Timothy Oppelt, Director
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ABSTRACT

The thermal decomposition properties of the active ingredient of 16 pesticides have been theoretically examined. The parameter used to rank their stability was the temperature required for 99% destruction at a gas phase residence time of 2.0 s under oxygen starved conditions.

Experimental studies on 5 pesticide related materials were also conducted under a controlled laboratory testing. Experimental studies of the high-temperature oxidation and pyrolysis of four key pesticide materials including the identification and quantification of products of incomplete combustion (PICs) were conducted. The four pesticides were: Aldicarb and Phorate (both insecticides), and Atrazine and Alachlor (both herbicides). These compounds are the active ingredients of Thimet, Temik, Aatrex-Nine-O, and Lasso II, respectively. A fifth material, a polyethylene blend bag which is used as an Atrazine container, was also examined.

The examination of the incineration ranking among the 16 subject pesticides indicated that they should be considered thermally fragile. However, each pesticide in the controlled laboratory testing decomposes to yield a large number of reaction intermediates. More intermediates were consistently produced under pyrolytic conditions. Most of the intermediates were decomposed by 700°C. Some persisted at the maximum temperature ,1000°C. It appears that these materials may be amenable to properly controlled, high-temperature incineration. It is clear that open-burning of spent pesticide bags may not significantly reduce their impact on the environment. It is also concluded that further development of the analytical protocols associated with the monitoring of decomposition products from pesticide materials should be conducted.

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SECTION 1

INTRODUCTION

Each year hundreds of thousands of pounds of pesticides, insecticides, herbicides, and fungicides are applied worldwide to control rodents, insects, weeds and fungi thought to be a direct threat to human health, or a threat to livestock and crops raised for human consumption (1). There has recently been renewed concern over the impact of applying these chemicals at an ever expanding rate, both to the environment and to people, whose quality of life these chemicals have been designed to enhance.

Many studies conducted to address these concerns have evaluated the persistence and toxicology of pesticide materials in soils and plant and animal tissues. These studies indicate that most pesticides themselves are fragile compounds that are readily transformed in the environment to other metabolites which may or may not be more toxic or more persistent than the parent material (2-8).

However, what happens when pesticides are thermally decomposed, as in the case of open burning of spent bag materials containing trace quantities of pesticides, as is a common practice for many farmers? Or, what occurs when a pesticide has been determined through 'persistence and toxicological' studies to no longer be suitable for widespread use and is suddenly banned? The method of choice for the disposal of these materials in many instances is incineration. How will these materials react upon thermal decomposition? A review of the open literature suggests that there is only limited information available (9-12).

Kennedy, et. al., conducted thermal degradation studies of 20 pesticide materials in the late 1970's: Atrazine, Bromacil, Carbaryl, Dalapon, DDT, Dicamba, Dieldrin, Diuron, Dinoseb, DSMA, Malathion, Nemagon, Paraquat, Picloram, PMA, Trifluralin, 2,4-D, 2,4,5-T, Vernam, and Zineb (9). The weight loss of each pesticide with increasing temperature was determined using a muffle furnace. Degradation studies of each pesticide were also conducted using sealed ampoules containing the pesticide so that the evolved gases could be subjected to mass spectral analysis. However, there was no attempt to separate the gases that entered the mass spectrometer (i.e., all gases were detected simultaneously), and identification was very crude by today's standards since compounds were only identified by presence of their characteristic fragments, and less than 10% of the tentatively identified compounds were subsequently confirmed. In addition, no attempt was made to analyze the solid residues that may have remained in the ampoule.

Turco, et. al., examined the thermal decomposition of 8 substituted 4,6-bis(alkylamino)s-triazines: 2-Chloro-4,6-bis-ethylamino-s-triazine (Simazine), 2-Chloro-4-ethylamino-6-isopropylamino-s-triazine (Atrazine), 2-Chloro-4,6-bis-isopropyl-amino-s-triazine (Propazine), 2-Methoxy-4-ethylamino-6-tert-butylamino-s-triazine, 2-Methyl-4,6-bis-isopropylamino-s-triazine, 2-Hydroxy-4,6-bis-ethylamino-s-triazine,

2-Hydroxy-4-ethylamino-6-isopropyl-s-triazine, and 2-Hydroxy-4,6-bis-isopropylamino-s-triazine (10). Thermogravametric Analysis (TGA), Differential Thermal Analysis (DTA), and Differential Thermal Gravimetry (DTG) techniques were used to determine the temperature at which the onset of decomposition began, as well as the overall decomposition profile. This data was used to determine their Arrhenius decomposition kinetic parameters. However, no attempt was made to identify the products of combustion.

Duvall, et. al., evaluated the thermal decomposition of Kepone, Mirex, and p,p'-DDT at 1 second residence time in air utilizing a quartz flow reactor (11). Decomposition profiles were determined, but only limited products were identified and verified using standards. This study showed that the pesticides were fragile, (i.e., decomposing to >99% by 700°C), while their products of incomplete combustion (PICs) were much more stable (persisting at >900°C).

Durig, et. al., examined the thermal decomposition of six organophosphorus compounds: Ethylphosphonic dichloride, Methylphosphonic dichloride, Ethyldichlorophosphine, Ethyldimethylphosphine, Dimethoxymethylphosphonate, and Ethylphosphonic difluoride (12). A pyrolysis-GC method was used to decompose the compounds and a flame ionization detector was used to quantitate the products. Decomposition pathways were proposed based upon the levels of decomposition observed at various pyrolysis temperatures; however, no products were identified.

In this study, we have theoretically examined the thermal decomposition properties of the active ingredient of 16 pesticides and conducted experimental studies on 5 pesticide related materials. The theoretical stability evaluations were prepared using available laboratory data, or data on structurally similar compounds in conjunction with chemical reaction kinetic theory (13). A summary of this work is presented in Table 1. The parameters used to rank their stability was the temperature required for 99% destruction at a gas phase residence time of 2.0 s under oxygen starved conditions, T_{99}(2). This parameter has also been used in a ranking of toxic organic compound incinerability (14). The table also indicates the thermal stability ranking and the thermal stability class ranking of each of the pesticides within the hierarchy of the 330 individual compounds and seven classes currently included in the list (a ranking of 1 being most stable). Data sheets on each pesticide are presented in Appendix 1.

This report focuses on detailed experimental studies of the high-temperature oxidation and pyrolysis of four key pesticide materials including the identification and quantification of products of incomplete combustion (PICs). The four pesticides were: Aldicarb and Phorate (both insecticides), and Atrazine and Alachlor (both herbicides). These compounds are the active ingredients of Thimet, Temik, Aatrex-Nine-O, and Lasso II, respectively. A fifth material, a polyethylene blend bag which is used as an Atrazine container, was also examined. Hopefully, the knowledge gained in these studies can be used to make more informed decisions concerning future handling of the pesticides.

TABLE 1. PESTICIDE THERMAL STABILITY DATA

Compound	$T_{99}(2)$(°C)	Ranking	Class Division
DCPA	750	105-114	3
Alachlor*	620	185-189	4
Acephate	595	207	5
Pronamide	570	220	5
Carbonfuran	560	226-228	5
Triallate	550	231-234	5
Fonofos	530	237-241	5
Ethoprop	530	237-241	5
Chlorprifos	510	249-251	5
Atrazine*	510	249-251	5
Terbufos	510	249-251	5
Cyanazine	500	253-258	5
Azinphos Methyl	460	266-269	5
Phorate*	400	276-277	6
Methomyl	200	318-320	7
Aldicarb*	200	318-320	7

* Derived from experimental data obtained from this study

SECTION 2

CONCLUSIONS

The experimental results of this study are very complex, full interpretation of which go far beyond the scope of this program. Some simple conclusions are, however, readily apparent.

1. Based on the stability of the parent pesticides and their thermal by-products, it appears that these materials may be amenable to properly controlled, high-temperature incineration. However, the number yields and stability of the by-products suggest that open-burning of spent bag materials containing pesticide residues may not significantly reduce their impact on the environment.

2. Based on comparison to results of a previously generated ranking of hazardous waste incinerability, the 16 subject pesticides (with the possible exception of DCPA) should be considered thermally fragile(i.e., $T_{99}(2) < 600°C$).

3. With the exception of Alachlor, there was almost no effect of reaction atmosphere on pesticide stability. This suggests that the primary mechanisms of decomposition are unimolecular (e.g., simple bond rupture or more complex concerted intramolecular reactions).

4. Each pesticide decomposes to yield a large number of reaction intermediates. More intermediates were consistently produced under pyrolytic conditions. Most of the intermediates were decomposed by 700°C, however, some persisted at the maximum temperature in this study, 1000°C. The most stable organic intermediates were primarily nitrogen containing compounds (i.e., nitriles and cyanides).

5. Relatively good mass balances were obtained for three of the pesticides, suggesting a reasonably complete set of product identifications.

6. Polyethylene bag oxidation intermediates did not appear to be as environmentally significant as the pesticide intermediates.

SECTION 3

RECOMMENDATIONS

Based on the complex chemistry observed in these studies it would be unwise to suggest that we can, on a theoretical basis, predict the by-products from the open-burning of pesticides not subjected to laboratory testing. The myriad of potentially toxic by-products that can be formed may represent an unsurmountable challenge if initial identifications are attempted in field tests prior to controlled laboratory testing. Due to the numerous by-products and complex chemistry observed as the results of the thermal degradation of pesticides, we offer the following recommendations:

1. Additional laboratory testing of other pesticide products suspected to be environmentally sensitive should be performed. Results of these studies can be used to evaluate the environmental impact of pesticide burning and guide larger scale evaluation programs.

2. Further development of the analytical protocols associated with the monitoring of decomposition products from pesticide materials should be conducted. Many of the by-products observed in our laboratory evaluations are polar and may be water soluble thus complicating their analysis. Standardized analytical techniques are not available for many compounds. This can result in a reduced tendency to analyze for these potentially environmentally significant species, although analytical techniques may already be available.

3. Thermal decomposition chemistry and kinetics of pesticides should be the subject of further research such that the open-burning and incineration behavior of pesticides may be better understood. Organic nitrogen and sulfur combustion chemistry are largely unexplored fields of apparent environmental significance.

4. Close coordination between laboratory researchers and field test researchers should be attempted to ensure that the products identified in the laboratory are targeted for measurement in the field.

5. Toxicological evaluation of the observed by-products should be performed to aid in the determination of the environmental risk associated with open-burning and incineration of pesticides.

SECTION 4

EXPERIMENTAL PROCEDURES

An exhaustive experimental study of the thermal degradation characteristics of four pesticides was undertaken. This included a successful atom balance for carbon, nitrogen, sulfur, phosphorus and chlorine.

4.1 INSTRUMENTATION

All experiments were performed on the Thermal Decomposition Analytical System (TDAS) which has been described in detail elsewhere (15). The TDAS is a closed, in-line quartz flow reactor system capable of accepting a solid, liquid or gas phase sample, exposing the volatilized sample to a highly controlled thermal environment, and then performing an analysis of the effluents resulting from this exposure.

Gas-phase samples are swept with carrier gas through heated transfer lines into a quartz flow reactor where controlled high temperature exposure occurs. Mean residence times of 0.5 to 6.0 seconds may be achieved. Thermal decomposition data may be taken over the temperature range 200 to 1050°C.

The effluent resulting from thermal exposure is swept by carrier gas to an HP 5890 GC where it is cryogenically focused on the head of a capillary column located inside the GC oven. Later, the oven temperature is raised at a specified rate and the separated compounds eluting from the column can then be sent to either the ion source of an HP 5970B mass selective detector (MSD), or to a flame ionization detector (FID) located within the GC assembly.

Data acquisition and analysis for the TDAS is accomplished with the aid of an HP 59970 ChemStation and the accompanying system software which includes an on-line NIH-EPA mass spectral library. Species with molecular weights between 16 g/mol (analytical unit limit) and 450 g/mol (transport limit of the thermal unit) may be analyzed using this system.

In order to successfully execute this ambitious program, it was necessary to develop a new interface between the GC and the MSD. This interface, the insertion-split, was designed as a compromise between the typically used 'direct-to-source interface' and the 'open-split interface', incorporating the meritous aspects of each. For example, the direct-to-source interface promotes heightened sensitivity for the mass spectrometer because eluents from the column are deposited directly into the source, just as the name implies. However, there are many limitations to this type of interface, one of which directly impacts the type work discussed here. Namely, having the GC column outlet placed directly in the source of the mass spectrometer (typically held at 10-6 or 10-7 torr) creates a huge pressure drop across the column which literally pulls volatile compounds through the latter portion of the column without allowing for any separation that may be attained by interaction with the liquid stationary phase. For these experiments it was paramount that there be separation of such compounds as CO_2, CH_4 and the light C_2 gases, since these were predicted to be major PICs.

The open-split interface provides for the use of much larger column bores and larger sample sizes, but protects the source of the mass spectrometer from undue wear and tear since much of the column effluent is diverted before it enters the source. One of the chief drawbacks of this type of interface is the loss of sensitivity relative to the direct-to-source interface. Since one of the goals of this study was to perform a mass balance of the data, it was imperative to isolate and analyze as many of the products as possible. The insertion-split interface provided the best answer to these two dilemmas.

Essentially the insertion-split interface is a small-bore transfer tube placed within a capillary column which is surrounded by carrier gas that is constantly being swept away. A drawing of this interface as it is installed in the TDAS is presented in Figure 1. A piece of narrow bore, fused silica tubing (uncoated but deactivated) is positioned in the source of the mass spectrometer in much the same way that the capillary column would be positioned if it were direct-to-source, with a fixed length left on the oven side of the connection nut (can be a variable length 10-20 cm). The end of this tubing remaining in the oven is then placed inside the outlet end of the GC capillary column. Obviously, attention must be paid to the inner and outer dimensions of the two tubes. The film thickness of the capillary column is also important relative to GC-MS operation. The ends of the transfer tubing and the capillary column which overlap are housed within a stainless steel piece of tubing fitted with inlet and outlet gas flows which allow a gaseous carrier to be purging the area surrounding the junction at all times. Finally, the entire stainless steel miniaturized housing is firmly mounted inside the GC oven so as to remain stationary even while the GC oven fan is running.

Because there is a finite annular gap between the outer wall of the transfer tubing and the inner wall of the capillary column, and as this junction is kept pressurized by the addition of flowing helium carrier surrounding the two overlapping tubes, the outlet to the capillary column now experiences approximately atmospheric pressure. Thus, light weight materials are not 'pulled' through the column without being separated as with the direct-to-source interface. Also, because the transfer tubing is placed inside the capillary column, transfer of sample from column to MS is almost continuous; there is no axial or open gap in the flowpath of the column effluent as would be experienced by the open-split interface. This fact helps to maintain relatively good sensitivity for this interface despite the fact that there is some splitting of the sample at the column overlap junction.

Before invoking the insertion-split interface for this program considerable developmental work went into testing the linearity of splitting for light weight as well as heavy materials (i.e., whether heavy materials would be preferentially split relative to light weight compounds because of the axial position they would tend to occupy while traveling through the capillary column). The insertion-split interface design used a bluff-body mixing principle at the annular split location as a contingency for this concern. Test results indicated that indeed the bluff-body design performed as expected; splitting of a wide-molecular weight test sample was consistently the same for light, intermediate, and heavy compounds. (The compounds used

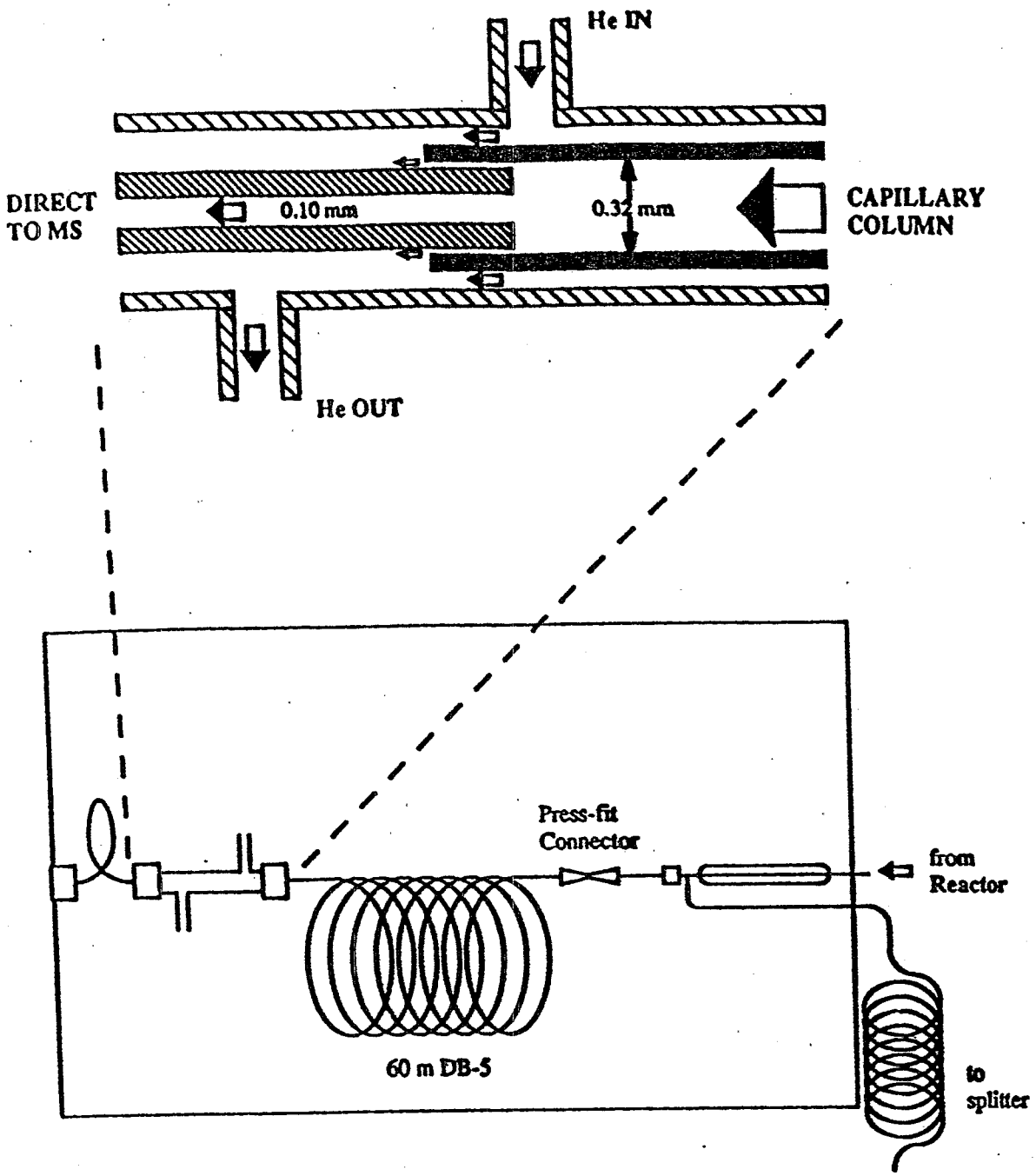


Figure 1. Close-up schematic of the insertion-split interface as it is configured in the TDAS.

were octane, octadecane, and octacosane in cyclohexane). We also found that for a given volumetric column flow, linear velocity and head pressure, the insertion-split interface response was always a fixed fraction (approximately 40-50%) of that experienced with the direct-to-source interface. This number is of course dependent upon the length and diameter of the transfer tubing positioned in the source of the mass spectrometer.

4.2 SAMPLE INTRODUCTION

Standards of each of four pesticides were received from the National Repository located at Research Triangle Park, North Carolina. The purity of each was certified as greater than 98% (i.e., Aldicarb 99.8%, Phorate 98.2%, Atrazine 99.4%, and Alachlor 99.6%). Aldicarb, Atrazine, and Alachlor were solids at room temperature, while Phorate was a viscous liquid. The structures of all four of the compounds are presented in Figure 2. A virgin Atrazine 90 DF bag (i.e., a bag which had seen no pesticide material) was received from the project officer.

Target test conditions for the four pesticide active ingredients were 1% mol/mol of pesticide in carrier gas, a gas phase residence time (tr) = 2.0 seconds, and two reaction atmospheres: pyrolysis at a fuel/oxygen equivalence ratio (phi) of 10; and oxidation at phi = 0.5 (100 % excess oxygen). The Atrazine bag material was run only under oxidative conditions. The stoichiometric combustion equations for each pesticide are given below. Equilibrium calculations using the STANJAN thermodynamic equilibrium code indicated that NO, SO_2, and PO_4 were the thermodynamically stable combustion end-products for N, S, and P under our experimental conditions (16).

Aldicarb (TEMIK)

$$C_7H_{14}N_{20}O_2S + 11.5\ O_2 \text{ ---> } 7\ CO_2 + 2NO + SO_2 + 7H_2O$$

Phorate (Thimet)

$$C_7H_{17}O_2PS_3 + 16.25\ O_2 \text{ ---> } 7\ CO_2 + 3\ SO_2 + PO_4 + 8.5\ H_2O$$

Atrazine (AA-TREX Nine O)

$$C_{14}H_{20}ClNO_2 + 18.25\ O_2 \text{ ---> } 14\ CO_2 + NO + HCl + 9.5\ H_2O$$

Alachlor (LASSO-II)

$$C_8H_{14}ClN_5 + 13.75\ O_2 \text{ ---> } 8CO_2 + 5NO + HCl + 6.5\ H_2O$$

Sample delivery for the three solid pesticide active ingredients (Aldicarb, Atrazine, and Alachlor) in this set of experiments involved dissolving the solid material in a suitable solvent and depositing an aliquot of the solution into a quartz pyroprobe tube. Once the solvent had evaporated the tube was placed in the platinum coil of a CDS Model 120 Pyroprobe assembly (Chemical Data System, Inc.) which was then placed into the insertion region

of the TDAS. Using temperature programming of both the insertion region itself and/or the pyroprobe heating coil, each pesticide was volatilized into flowing carrier gas at a specific, reproducible rate (for a given programming protocol). Separate TGA experiments were performed in flowing air and nitrogen to aid in determining the first approximation of these temperature protocols.

Before each pesticide series was to begin, approximately 40 quartz tubes were loaded with sample from the same stock standard solution and solvent was allowed to evaporate. The tubes were then kept covered at room temperature in a laboratory hood until just prior to use. It was determined that loading the quartz tubes in this manner provided the best reproducibility with regard to sample size.

Sample delivery for the only liquid active ingredient, Phorate, was more straightforward than for the three solids. 0.5 ul of the pure liquid was injected into an insertion region held isothermally at 100°C using a 0.5 ul full-scale liquid syringe fitted with a 6 inch needle.

The polyethylene bag was run as follows. Approximately 2 mg of bag material was placed in a quartz pyroprobe tube (loaded with a plug of quartz wool to keep the piece of polymeric material from falling out). The tube was then placed in the platinum coil of the CDS Pyroprobe assembly and placed into the insertion region of the TDAS. As with the solid pesticides, temperature programming of both the insertion region itself and the pyroprobe heating coil volatilized the sample into flowing carrier. A separate TGA experiment was performed in flowing air to aid in determining the first approximation of this temperature protocol.

The profiles generated using these sample introduction techniques delivered the maximum possible ppm (mol/mol) concentration of pesticide in the carrier gas while also delivering a suitable sample size to the analytical system downstream of the reactor for adequate conversion to products. The concentration of active ingredients ranged from 0.1 to 0.5% mol/mol in the carrier, with the sample sizes ranging from 77 to 500 ug. Table 2 presents a summary of the pesticide concentrations in carrier gas utilized in this study, the insertion region protocols which delivered these values, and the accompanying oxygen concentrations required for phi = 0.5.

Degradation of each of the three pesticides was conducted under both oxygen deficient (fuel/oxygen equivalence ratio of 10) and oxygen rich (fuel/oxygen equivalence ratio of 0.4 - 0.5) conditions. Approximately 0.5% oxygen in helium (mol/mol) was available for combustion in the oxygen deficient conditions (as determined by actual measurement of the reaction gas), whereas a 10% mix of oxygen in a balance of 51% helium/39% nitrogen was used for the oxygen rich experiments (these were the values obtained by mixing compressed air and helium at a one to one ratio vol/vol). Gas mixtures were prepared by utilizing a gas mixing device developed in-house. Residence time at temperature for all exposures regardless of atmosphere was held constant at 2.0 seconds, while the reactor temperature was varied over the range 200-1000°C. Experiments were conducted at 1.23 atm. Sample introduction was

accomplished using the protocols described in the proceeding paragraphs.

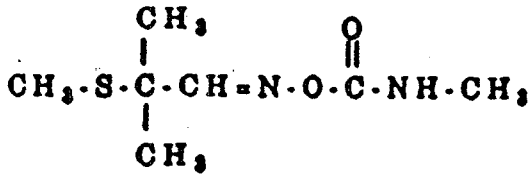
The effluent resulting from a single reactor exposure (unreacted parent material and all PICs) was directed to a 60 m, DB-5, 0.32 mm i.d. column (J&W Scientific, Inc.) held at -60°C, using liquid nitrogen as coolant. Individual reaction products were separated by programming the GC oven from -60 to 290°C @ 10°C/min with a 15 minute hold at -60°C and a 25 minute hold at 290°C. Detection was accomplished with the aid of an HP 5970B quadrapole mass spectrometer. The mass spectrometer was operated in full-scan mode with an electron energy of 70 eV and an electron multiplier setting of 1700. To optimize detection of products, the mass range scanned during the first 20 minutes of the GC program was 10-200 amu, while from 20-80 minutes the mass range scanned was 10-500 amu. This allowed for maximum detection of light gasses during the first part of the GC program. Quantitation and identification of products was performed with the aid of an HP ChemStation data system and an on-line NIH-NBS mass spectral library as well as through manual interpretation.

Analytical standards for observed products were run wherever possible to obtain quantitative response factors. Where obtaining a product was either impossible, extremely difficult, or untimely (i.e., a 6 week or 2 month waiting period), analytical standards were run for compounds which were in the same class, or closely related in structure to the compound of interest. These response factors were then used to estimate the response factors for the actual products seen in thermal decomposition experiments. Response factors were typically obtained from 4 or 5 point calibration curves with some replicate points being performed where possible.

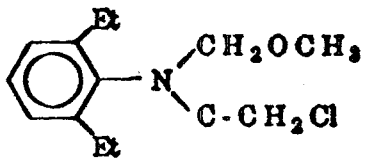
Standards were injected into the TDAS using the same timetable, valve switching, split ratio, and GC program as were the pesticides. Thus, response factors generated from the curves could be used directly to perform absolute quantification of the area responses reported in each data run using the following equation:

Ng of compound detected = Area Counts of compound/response factor

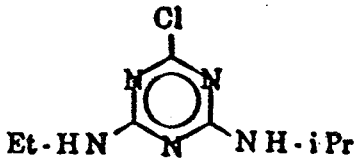
The 'ng detected' values were then converted using molecular formulas and molecular weights to yield mass and/or moles of carbon, nitrogen, sulfur, phosphorus and chlorine. In this way a balance of the atoms at each temperature could be evaluated. The compiled list of analytical standards run for this program and the response factors determined in both reaction atmospheres are given in Appendix 2.



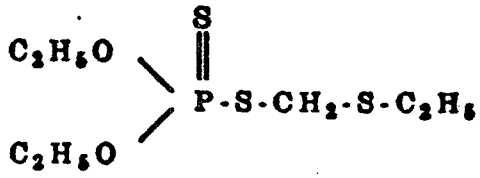
ALDICARB (Temik® Insecticide)



ALACHLOR (Lasso-II® Herbicide)



ATRAZINE (Aatrex-Nine-O® Herbicide)



PHORATE (Thimet® Insecticide)

TABLE 2. VOLATILIZATION PARAMETERS AND CONCENTRATION OF O_2 IN THE CARRIER UTILIZED TO ACHIEVE TARGET TEST CONDITIONS

Compound	Insertion Region Program	Pyroprobe Program	Conc. (mol/mol)	Pyrolysis		Oxidation	
				% O_2* in Carrier	phi+	% 0_2 in Carrier	phi
Aldicarb/s‡	Isothermal @ 200°C	No Program	4000	0.5(0.5)	10(10)	10(9)	0.5(0.5)
Phorate/1	Isothermal @ 100°C	Not used	5000	0.5(0.5)	10(10)	10(7)	0.4(0.5)
Atrazine/s	Isothermal @ 275°C	Ambient to 275°C @ 20°C/ms hold 20s	3000	0.5(0.5)	10(10)	10(10)	0.5(0.5)
Alachlor/s	Isothermal @ 300°C	Ambient to 300°C @ 20°C/ms hold 20s	4000	0.5(0.5)	10(10)	10(8)	0.5(0.5)
Atrazine DF bags	Isothermal @ 250°C	Ambient to 500°C @ 20°C/ms	Not applicable§	0.5	Not applicable	10	Not applicable

*Concentration of oxygen mol/mol in carrier required for complete combusion based upon the stoichiometric equation for the pesticide, listed as: actual (theoretical).

+Phi value for the oxidative experiments listed as: actual (theoretical).

‡"s" indicates solid phase sample, "1" indicates liquid phase sample.

§No attempt was made to calculate a "concentration" or "phi" value for the polymer.

SECTION 5

RESULTS

As expected, the chromatograms generated in this study were very complex, especially at intermediate destruction temperatures. For example, the thermal decomposition of Alachlor under oxygen deficient conditions yielded > 80 different PICs over the temperature range of 275 - 1000°C. This was the largest number of products formed from an individual compound that our laboratory has ever observed. A typical example chromatogram obtained from the Alachlor experiments is presented in Figure 3.

While the excess oxygen chromatograms were generally less complex than the pyrolysis ones, a relatively large number of products were nevertheless detected in these experiments as well. The number of by-products observed for each of the pesticides is summarized in Table 3.

TABLE 3. NUMBER OF DECOMPOSITION BY-PRODUCTS OBSERVED

Pesticide	phi = 10	phi = 0.4-0.5
Aldicarb	39 (23)	22 (17)
Phorate	31 (19)	25 (17)
Atrazine	63 (50)	47 (36)
Alachlor	86 (59)	29 (23)

( ) indicates the number identified by the mass spectra, remainder listed as unidentified

The metabolite studies found in the literature reported that these four pesticides were not persistent in the environment and that they were readily transformed to other compounds (2-10). Their thermal stability as determined under the conditions of this study was analogous to this behavior. All four compounds themselves were labile, disappearing by 600°C under both pyrolytic and oxidative conditions. The relative stabilities can be conveniently ranked by the temperature required for 99% destruction for a 2.0 second residence time ($T_{99}(2)$) (see Table 4). The relative stabilities under both sets of conditions in this study were: Alachlor > Atrazine > Phorate > Aldicarb.

Aldicarb and Phorate exhibited degradation at the lowest reactor temperature possible on the TDAS, 200°C. Because no Aldicarb was detected in the quantitative transport run at 200°C (i.e., it had already been converted to products), this temperature was assigned as its $T_{99}(2)$ value. In

the case of Phorate, the $T_{99}(2)$ value is the temperature at which no Phorate was detected in replicate runs. The detection limit for this compound was approximately 0.4 % remaining. A more in-depth explanation of the problems associated with running Phorate are discussed in the following section of this report.

TABLE 4. PESTICIDE STABILITY

	$T_{99}(2)$ (°C)	
Pesticide	phi = 10	phi = 0.4-0.5
Aldicarb	<200	<200
Phorate	<400	<275
Atrazine	510	475
Alachlor	620	525

It is interesting to note that none of the pesticides displayed a large dependence upon reaction atmosphere. This observation infers that the decomposition mechanisms may be dominated by unimolecular pathways. A more pictorial representation of this can be seen in the thermal decomposition composite curves generated for the pesticides, Alachlor and Atrazine, in Figure 4.

Tables 5 through 10 present the specific products detected in the decomposition studies of Aldicarb, Atrazine, and Alachlor in the form of Weight % Yield (relative to parent) for each atmosphere. Many of the products detected in these experiments may be environmentally significant.

Due to the viscosity of Phorate, the small volume available for sampling (i.e., only 50 ul in a 1.5 mL vial volume), and the short 'shelf-life' of Phorate once exposed to the atmosphere, the reproducibility of injection was not good. Replicate and triplicate injections at each reaction condition resulted in relative standard deviations of as much as +- 36%. For this reason, only qualitative analysis of the Phorate decomposition products are listed in Tables 11 and 12. All areas of peaks that were not identifiable by their mass spectra are summed under the heading 'Unidentified'.

Results obtained from the Atrazine bag oxidation experiments are presented in the same manner as Phorate data in Table 13 (i.e., as qualitative analysis of the decomposition products). The act of volatilizing the polymer in the insertion region necessarily makes 'Weight % Yield (relative to parent)' type data meaningless. As with Phorate, areas of peaks which we were unable to identify are summed under the heading 'Unidentified'. The products seen from this series of experiments were the same ones observed in previous

studies conducted in this laboratory in which polyethylene and polyethylene/polypropylene blends were thermally decomposed (17).

Mass balance for the pesticide experiments was achieved with a fairly good degree of success. Some temperature data points were clearly outliers, while most data points were within +- 30% of the 100% recovery mark. A listing of the atom balances for C, N, S, or Cl where appropriate are presented in Appendix 3. Because of the high degree of uncertainty associated with the Phorate data, no atom balances were attempted.

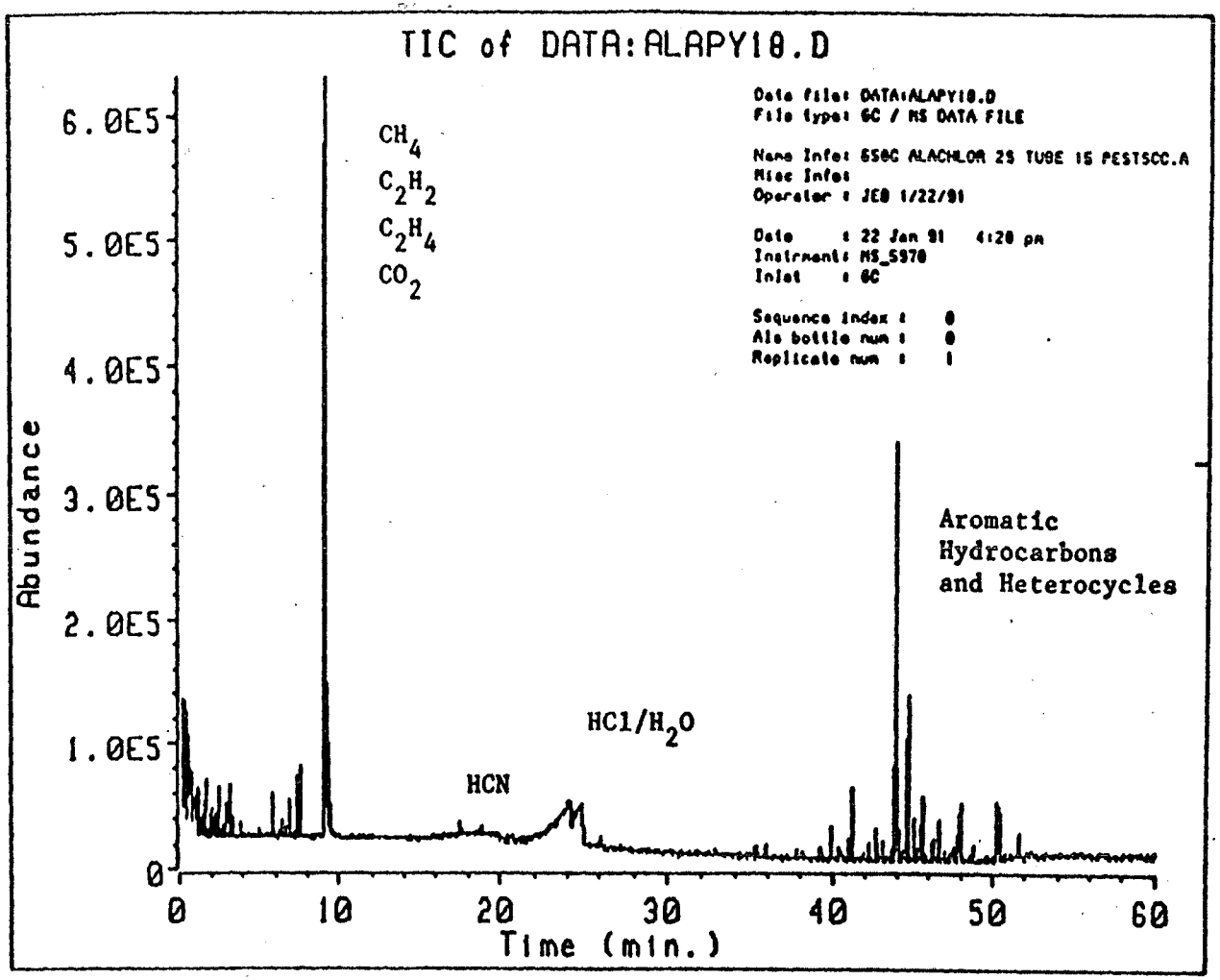


Figure 3. Example chromatogram generated for Alachlor pyrolysis, phi=10, 4000 ppm, 2s residence time, 1.23 atm.

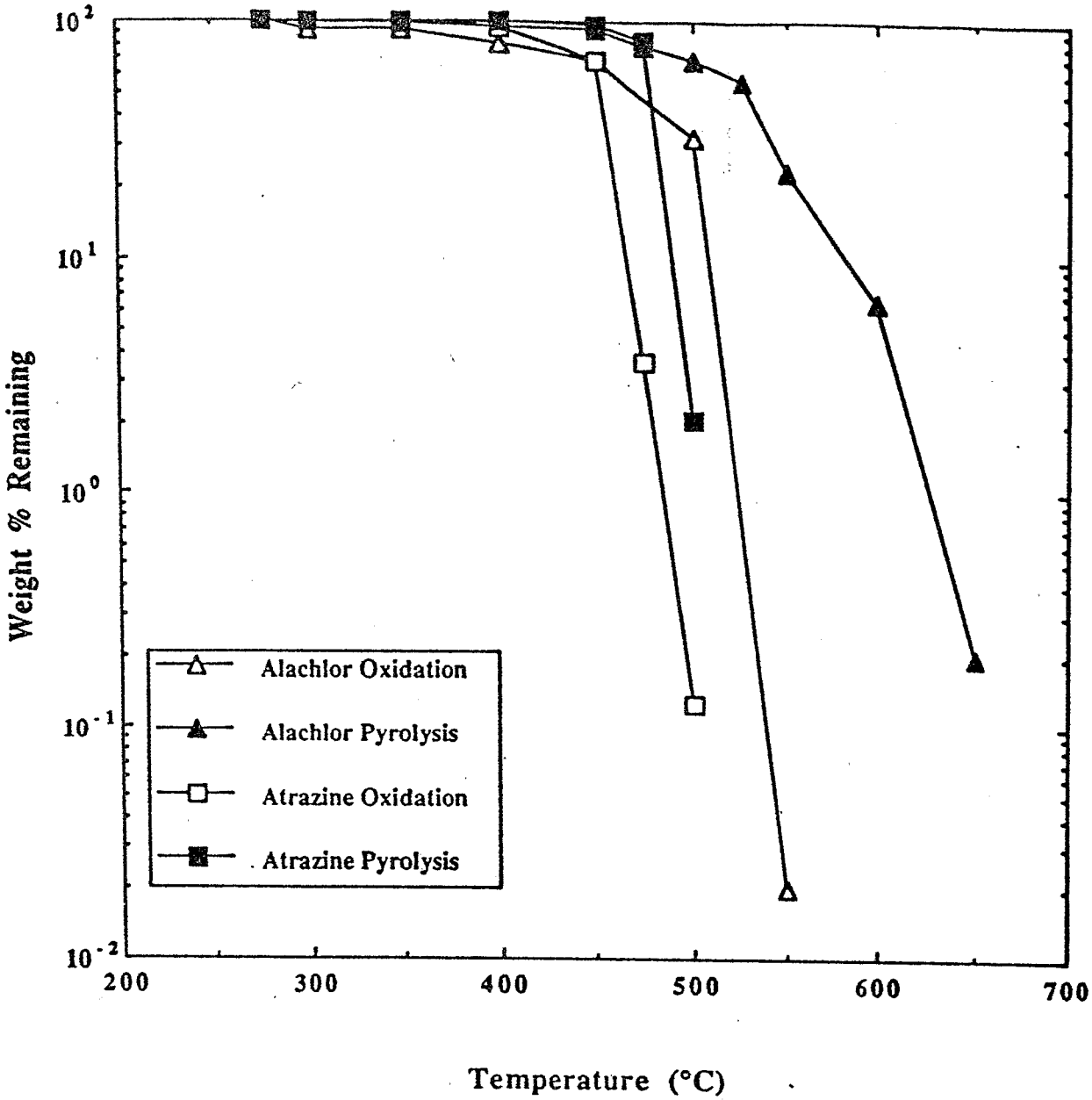


Figure 4. Weight % remaining curves for parent materials, Alachlor and Atrazine, generated under oxidative (phi = 0.5) and pyrolytic (phi= 10.0) conditions, 2.0 sec residence time, 4000 and 3000 ppm respectively, and 1.23 atm.

TABLE 5. WEIGHT % YIELD OF PRODUCTS DETECTED IN ALDICARB OXIDATION

		Temperature (°C)								
Compound	Molecular Formula	275	300	350	400	450	500	550	600	650
Acetone	C3H6O	1.18								
2-Methyl-2-propenenitrile	C4H7N	0.53	0.67	1.46	2.32	16.27	14.76	16.11	4.53	
Methyl-thio-propene	C4H8S	2.72	1.66	1.54	4.48	10.67	2.24			
C5H11N isomer	C5H11N	6.52	7.36	3.68	5.00					
Dimethyldisulfide	C2H6S2	0.83	1.29		0.52					
C5H9NS isomer	C5H9NS	160.14	140.05	146.25	105.18	45.82	1.52			
C5H11NOS isomer	C5H11NOS	5.50	3.47	2.92						
Unidentified		1.07								
Unidentified		1.13	0.15							
Carbon dioxide	CO2	4.28	3.13	14.14	4.24	5.90	4.51	4.84	7.45	11.53
NO	NO	2.02	4.04	0.00	8.08	0.31	1.98	0.99		
Unidentified			2.37	0.48	1.47	1.38				
Unidentified			0.41							
Unidentified			0.67		0.27					
Isocyanatomethane	C2H3NO		0.06			8.41	2.35	1.64		
Hydrogen azide	HN3			2.34				1.43	3.33	5.81
Sulfur dioxide	SO2					9.81	21.21	38.44	37.93	44.18
Hydrogen cyanide	HCN					8.00	9.78	14.92	26.41	14.03
C3H3NO isomer	C2H2NO					1.27				
Carbon monoxide	CO						40.40	80.81	101.01	121.21
2-Propenenitrile	C3H3N							0.94	2.09	

TABLE 6. WEIGHT % YIELD OF PRODUCTS DETECTED IN ALDICARB PYROLYSIS

		Temperature (°C)														
Compound	Molecular Formula	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
Isocyanatomethane	C2H3NO	0.67	0.89	0.94			0.40									
Acetone	C3H6O	1.64			1.39	0.23	0.62	4.34	6.64	0.57	0.71	0.95				
2-Methyl-2-propenenitrile	C4H7N	0.37	0.08	1.52	9.00	45.42	50.02	46.81	29.45	24.27	19.48	7.07	0.63	0.14		
Methyl(thio)-1-propene	C4H8S	2.42		2.13	5.40	5.97	0.36									
Dimethyl disulfide	C2H6S2	0.44	0.02	0.54	3.58											
N,N'-Dimethylurea	C3H8N2O	2.31	1.88	1.92	1.40											
Carbon Monoxide	CO									20.20	20.20	20.20	20.20	40.40	16.16	10.10
Carbon dioxide	CO2															39.01
Unidentified		0.59			0.14											
Unidentified		0.28	0.06	0.25	0.36											
C5H9NS	C5H9NS	80.81	67.62	78.81	45.15	2.45										
Methanethiol	CH4S			0.87	4.60	24.20	10.93	1.88								
Unidentified				0.16	0.34											
Unidentifed				0.58	1.13											
Unidentified				0.32	2.96	2.55										
Unidentified																
2-Methylpropanenitrile	C4H9N				0.48	3.14	3.45	2.32	0.81							
2,2-Dimethylpropanenitrile	C5H9N				0.49	2.90	5.18	2.72	2.05							
N-Methyl-acetamide	C3H7NO				0.40	1.35	0.47									
Hydrogen Sulfide	H2S					1.70	1.58	2.32	1.09	1.79	2.35	1.96	1.05		0.89	1.16
Hydrogen cyanide	HCN					5.07	5.85	9.96	14.00	23.80	28.67	29.77	25.12	23.57	22.61	15.65
Thiobis-methane	C2H6S					1.03	1.71	1.39								
Carbon disulfide	CS2					1.03	4.03	7.75	9.73	16.90	21.63	22.80	22.63	12.80	12.32	7.65
Methane	CH4					1.44	3.75	4.62	5.77	9.24	10.39	12.12	9.24	5.57	5.77	2.31
Unidentified						0.97										
Unidentified						0.47	0.25									
Ethene	C2H4						2.02	2.83	2.83	4.04	3.23	5.05	4.84	2.32	1.62	0.19
Sulfur dioxide	SO2							0.68	6.79	11.39	10.56	11.28	10.83	9.87	6.06	6.99
Unidentified								0.30	0.23	0.40						
Ethyne	C2H2									0.51	1.06	1.77	3.54	4.94	5.30	4.50
Benzonitrile	C7H5N										0.34	1.58	2.82	0.86	1.13	0.59
Unidentifed											1.59	1.89	2.49	5.39	1.07	
Unidentified											1.04	2.17	3.02	1.49	1.57	1.26
Butanedinitrile	C4H2N2											0.38	0.82	0.22	1.35	

TABLE 7. WEIGHT % YIELD OF PRODUCTS DETECTED IN ATRAZINE OXIDATION

		Temperature (°C)											
Compound	Molecular Formula	300	350	400	450	475	500	550	575	600	650	700	800
2-Chloro-4,6-bis-isopropyl-amino-s-triazine	C9H16N5Cl	0.46	0.71	0.07									
C8H14N5Cl isomer	C8H14N5Cl		0.11										
2,6-Bis-(1-methyl-ethyl)-benzeneamine	C12H19N			0.46	6.30	5.36	1.53	0.83	0.40				
4-Chloro-2,5-dimethoxy-benzeneamine	C10H14NO2Cl			0.42	7.17	1.22							
1-Propene	C3H6				2.28	2.11	2.92	3.05	1.64				
Ethanodinitrile	C2N2				3.50	2.20	2.17	3.48	3.64	5.24	6.77	8.11	0.68
Hydrogen cyanide	HCN				9.88	13.14	10.41	31.73	41.17	27.84	68.68	73.79	22.65
Hydrogen azide	HN3				3.23	1.93	2.38	4.21	7.83	7.43	13.68	12.95	2.64
Hydrogen chloride	HCl				3.01	8.00	4.00	18.88	16.55	16.16	16.31	16.62	17.28
2-Propenal	C3H4O							0.94	3.04	10.91			
Acetonitrile	C2H3N				8.41	4.79	5.28	10.03	11.69	6.16	3.80	0.35	
Acetone	C2H6O				1.10	1.89	2.64	1.32	2.83	0.09			
Isocyanatoethane	C3H5NO				1.42	1.83	0.79						
Propanenitrile	C3H5N				1.79	1.40	1.44	2.46	1.80	0.22			
2-Isocyanatopropane	C4H7NO				1.66	0.42		0.53					
3-(1-Methyl-ethyl-)oxetane	C6H12O				0.83	1.01	1.77	2.46					
Cyclobutanone	C4H6O				3.55	3.62	3.36	3.58	7.92	4.33	6.76	1.88	
1-Cyclo-propyl-ethanone	C5H8O				1.67	1.45	0.88						
1-(1,3-Dimethyl-3-cyclohexene-1-ethanone	C10H16O				0.31	0.36	0.75	1.07	0.26				
4-Methoxy-N-methyl-benzeneamine	C8H11NO				1.11	1.09	0.63						
3-Ethyl-2,5-dimethyl-pyrazine	C8H12N2				1.28	2.14	1.94	2.66	2.41	0.93			
2-Methoxy-3-1-methyl-ethyl-pyrazine	C8H12N2O				5.74	3.96	2.06						
3-Ethyl-4-hydroxy-6-methyl-2H-pyran-2-one	C8H10O3				1.47								
C6 Alkyl benzene	C12H18				1.07	1.66	1.18	0.31					
C6 Alkyl benzene	C12H18				0.28	0.22							
Unidentified					2.62								
Carbon dioxide	CO2					0.76	0.67	2.35	1.94	3.24	4.53	4.27	31.04
Carbon monoxide	CO					14.66	13.93	6.97	13.94	8.29	13.57		
2-Methyl-propanenitrile	C4H5N					0.25	0.55	1.01	0.77				
2,6-Diamino-4-1H-pyrimidinone	C4H6N4O					0.42	0.24						
6-Methyl-1H- purine	C6H6N4					0.51	0.52	1.91	0.54				
C6 Alkyl benzene	C12H18					0.52	0.26						
1,2-Dimethyl-4-phenyl-methyl-benzene	C15H16					1.42	0.54						
Unidentified						0.41							
Unidentifed						0.78	0.44	0.17					
Unidentifed							0.01						
Unidentifed							0.28						
Unidentifed								1.39					
1,3,5-Heptatrienoic acid	C7H8O2							0.44					
Unidentifed													
Unidentifed								0.20					
Unidentifed								4.96					
Unidentifed								0.36	0.28				
Propanenitrile	C3H3N								2.80	2.36	2.45	0.44	
Nitrous oxide	N2O									0.07	0.14	0.15	0.51
2-Oxo-propanenitrile	C3H3NO									0.24			

TABLE 8. WEIGHT % YIELD OF PRODUCTS DETECTED IN ATRAZINE PYROLYSIS

Compound	Molecular Formula	Temperature (°C) 400	425	450	475	500	525	550	600	650	700	750	800	850	900	950	1000
2,6-Bis-(1-methyl-ethyl-)benzenamine	C12H19N	0.47	3.35	6.05	4.88	4.31	3.71	3.00	0.26								
Acetonitrile	C2HN		0.71	2.16	3.49	5.48	6.06	9.11	6.79	5.92	3.81	2.77	4.32	7.12	4.45	1.71	0.09
Methyl-cyclo-pentene	C6H10		0.83	1.46	1.39		3.32										
Methyl-ethyl-oxetane	C6H12O		0.32	2.06	3.95	6.19	4.58										
Cyclopropylethanone	C5H8O		0.94	1.67	0.14	1.43	0.64										
Hydroxy-methoxy-benzene	C7H8O2		0.47	3.97	0.72												
C6 unsaturated	C6H14		1.29	1.05	0.63												
Ethylene	C2H4			0.09	0.09	0.16	0.25	0.57	0.52	0.94	0.95	0.28	0.21	0.28	0.09	0.06	
Hydrogen cyanide	HCN			2.19	10.93	19.21	18.43	26.73	23.77	38.92	63.88	63.81	74.02	80.16	83.66	64.07	68.91
Isocyanatoethane	C3H5NO			0.32	0.35												
Propanenitrile	C3H5N			0.09	0.76	1.64	1.89	2.58	1.14	0.88	0.25	0.08					
2,2-Dimethyl-propanenitrile	C5H9N			0.58	1.39	1.91	2.73	7.18	3.27	1.18	0.66						
2,6-Pyridinediamine	C6H7N3			0.40	1.40	0.34	4.90	5.17									
4-Methoxy-N-methyl-benzene	C8H11NO			0.34	0.87	1.51	0.83										
C6 Alkyl benzene	C12H18			0.95	2.57	5.70	5.48	1.93									
alpha-Methyl-N-pentenyl-benzenemethanamine	C9H13N			1.10	0.48												
Carbon Dioxide	CO2				0.16	0.37	0.46	3.00	2.81	2.70	1.36	1.98	0.49	1.05	1.61	2.73	1.85
1-Propene	C3H6				0.45	1.26	0.93	1.10	0.85	0.28							
Hydrogen Azide	HN3				2.43	1.10	1.10	3.52	6.17	7.62	5.68	3.33	3.73		2.78	0.85	0.28
Acetone	C3H6O				0.14	0.61	1.09	1.68									
2-Methyl-Propanenitrile	C4H7N				0.12	0.51	0.74	1.14	0.38	0.32							
Ethyl-dimethyl-pyrazine	C8H12N2				0.81		2.01	2.53	0.46								
C6 alkyl benzene	C6H18				0.38												
1-(1-Pentenyl-)piperidine	C10H19N				1.59												
Ethoxy-methoxy-benzene	C9H12O2				8.78	9.96	4.49	1.35									
6-Methyl-1H- purine	C6H6N4				0.38	0.83	1.61	1.44	0.33								
C6 Alkenyl benzene	C12H16				0.74	1.39	0.97	0.47									
3-Ethyl-4-hydroxy-6-methyl-2H-pyran-2-one	C8H10O3				1.78	1.92	0.81										
2 Benzene rings + CH3	C13H14				5.90	1.75	0.70		0.56								
Unidentified					0.23	0.62											
Unidentified					0.21												
2-Propynenitrile	C3HN				10.00	10.00	10.00	20.00	8.00	9.40	13.64	11.33	16.22	16.67	24.47	12.16	16.91
Cyanogen	C2N2					0.22	0.04			0.15	0.20	0.10	0.21	0.11			
4,5-Diamino-6-methyl-pyrimidine	C5H8N4					1.98	2.86										
Unidentified						2.45											
Unidentified						0.92											
C8H11NO2 isomer	C8H11NO2					0.40											
Unidentified						1.21											
Unidentified						0.30											
Unidentified						0.15											
Unidentified						1.32											
4,6-Dimethyl-2-pyrimidinediamine	C6H12N4						0.12										
2,5-Dimethyoxy-benzenamine	C8H11NO2						0.17										
Methoxy-methyl-ethyl-pyrazine	C8H12N2O						0.49										
Unidentified							1.04										
Unidentified							0.00	2.54									
Unidentified							0.26										
Unidentified							0.43										
2-Propenenitrile	C3HN						0.43										
2-Methyl-2-propenenitrile	C4H5N								0.58	1.77	3.28	2.99	4.49	3.69	2.65	0.46	0.20
2-Butenedinitrile	C4H3N									0.21							
Methane	CH4									0.23	0.36	0.20	0.42				
Acetylene	C2H2										0.26	0.52	0.46	0.40	0.57	0.33	0.24
Benzene	C6H6										0.01	0.07	0.06	0.13	0.23	0.16	0.11
2,4-Pentadienenitrile	C5H5N										0.29	0.58	1.07	1.98	1.42	0.83	0.66
Methyl-butenenitrile	C5H7N										0.06						
Methylene-propanedinitrile	C4H2N2								0.22	0.20	0.00						
Benzonitrile	C7H5N										0.11						
Hydrogen Chloride	HCL										0.19	0.30	0.28	1.41	1.57	1.24	0.70
Naphthalene	C10H8													3.47	0.56	0.32	0.29
Naphthalenecarbonitrile	C11H7N													0.24	0.28	0.23	0.22
1-Propyne	C3H4													0.25	0.15	0.32	0.17
Carbon Monoxide	CO													0.13			

TABLE 9. WEIGHT % YIELD OF PRODUCTS DETECTED IN ALACHLOR OXIDATION

Compound	Molecular Formula	Temperature (°C) 275	300	350	400	450	500	550	600	650	700
2-Chloro-2',6'-diethyl-acetanilide	C12H16NOCl	6.21	5.32	5.41	5.76	4.36	10.15	5.71			
Unidentified		0.21	0.37								
Methoxy-dimethyl-indole	C11H12NO		0.54	0.45	0.29		1.77	4.29	1.68		
2,6-Diethyl-benzeneamine	C10H15N		0.25	1.07	4.78	4.99	12.92	1.20			
Ethylquinoline	C11H11N		0.25		0.37	0.37	2.78	4.36	1.76		
Methoxy-dimethyl-indole	C11H12NO				0.47	0.51	0.51				
Acetic acid, chloromethyl ester	C3H5O2Cl				1.18	3.58	11.02	9.08	2.75		
2,6-Diethyl-benzonitrile	C9H13N				0.39	0.96	8.19	17.02	7.95		
Methyl-ethyl-quinoline	C12H13N				1.20	1.44	7.82	5.25	0.39		
Dihydro-dimethyl-1(2H)- Naphthalenone	C12H14O				0.12		0.70				
4,6-Dimethoxy-1,2-naphthoquinone	C12H10O4				1.26	2.51	13.28	5.96			
Carbon Dioxide	CO2				1.27	1.37	1.49	3.15	4.30	5.34	8.98
Nitric oxide	NO				0.21	0.99	1.28	0.04			
Hydrogen chloride	HCl					2.22	3.33	7.27	10.86	13.22	12.44
Ethyl-methyl-quinoline	C12H13N						0.64	0.59			
Phenyl-ethenyl-benzonitrile	C15H11N						0.27	0.16			
Substituted naphthalenone	c12H11O						0.66				
Unidentified							0.08				
Ethylquinoline	C11H11N						1.16		2.83		
Isocyanatonaphthalene	C11H7NO							1.01	3.35	2.22	
Methoxyacetaldehyde	C3H6O							1.39			
Unidentified								0.27	0.17		
Carbon monoxide	CO							17.78	66.67	88.89	111.11
Unidentified									0.43		
Unidentified									0.25		
Hydrogen cyanide	HCN									4.36	3.53
Hydrogen Azide	HN3									3.76	2.48
2-Propenenitrile	C3H3N									0.94	
Benzonitrile	C7H5N									0.65	

TABLE 10. WEIGHT % YIELD OF PRODUCTS DETECTED IN ALACHLOR PYROLYSIS

Compound	Molecular Formula	Temperature (°C) 300	400	450	475	500	525	550	600	650	700	750	800	850	900	950	1000
2-Chloro-2',6'-Diethylacetanilide	C12H16NOCl	0.69	0.83	1.81	2.74	3.47	9.77	6.92	1.04								
2,6-Diethylbenzenamine	C10H15N		2.02	4.71	7.59	15.98	12.79	5.36									
Acetic acid, chloromethyl ester	C3H5O2Cl			0.42	1.58	6.36	7.11	5.14	2.28								
2,6-Diethyl-benzonitrile	C11H13N			0.44	1.56	5.39	11.86	15.10	32.06	20.00	0.80						
2-Ethyl-4-methyl-quinoline	C12H13N			0.55	1.18	4.99	6.97	5.35	3.11	0.61	0.32						
2-Chloro-2'-propyl-6'-ethylacetanilide	C13H18NOCl			1.49	2.14	6.78	7.57	3.76	0.71								
Methane	CH4				0.26	0.53	5.01	5.27	8.97	10.02	7.28	6.86	9.49	11.92	12.68	12.13	12.04
NO	NO				0.22	0.51											
Substituted indole					0.39	1.71	2.27	3.41	11.36	7.01							
Ethyl-quinoline	C11H11N				0.72	1.49	2.13	2.65	0.00	2.96							
Methyl-ethyl-quinoline	C12H13N				0.17	0.50	0.97	0.72	1.21	0.61	0.25						
N,N-3,5-Tetramethylbenzenamine	C10H15N				0.82	1.47	1.08	1.21	0.61								
Acetylene	C2H2					0.15	0.50	0.75	2.01	5.02	1.00	6.03	4.02	2.01	4.93	7.53	9.04
C5 Alkyl benzene	C11H16					0.42	0.99	0.67	1.86								
5-Methoxy-2-methyl-1H-Indole	C10H13NO					0.61	0.69	0.61									
Chloromethane	CH3Cl						0.34	0.74	2.73	1.40	1.13	0.63					
Hydroxyacetaldehyde or methanol	CH4O						2.43	2.19									
Hydrogen chloride	HCl						0.91	2.34	13.84	14.85	12.66	11.60	9.28	10.46	12.62	13.48	12.76
1,2-Propanediol	C3H8O2						0.68	0.69	1.23								
Substituted indole	C10H12N						0.58	0.45									
Unidentified							0.06	0.30	2.69	0.78							
Unidentified							0.37										
Unidentified							0.17	0.39	0.18								
Unidentified							0.23										
Unidentified							1.45										
Ethene	C2H4							0.79	1.32	4.40	5.27	12.75	8.79	11.87	3.54	1.32	
Carbon dioxide	CO2							6.38	16.29	15.48	24.02	21.10	20.87	37.83	25.33	23.97	22.85
Nitrous oxide	N2O							0.37	0.52								
Ethyl-quinoline	C11H11N							0.38	3.37	6.66	1.09						
Isocyanonaphthalene	C11H7N							0.64	1.32	3.32	4.73	4.72	1.44				
Unidentified								0.40									
Acetone	C2H6O								0.60								
Diethylbenzene	C10H14								0.52								
1-Ethenyl-4-ethyl benzene	C10H12								1.00	1.14	0.84						
Tetrahydro-methyl quinoline	C10H10N								0.70	0.80	0.30						
3,5-Xylylisocyanide	C9H9N								1.02	2.31	1.41						
Substituted indole	C10H12N								2.80								
Ethyl-dimethyl-quinoline	C13H15N								0.31	0.88							
Unidentified									0.32	2.93	2.29	0.80					
Unidentified									1.26	0.55	0.00						
Unidentified									0.68	0.67	0.96						
Unidentified									1.65								
Unidentified									0.80								
Unidentified									0.53	0.69							
Unidentified									0.23	0.00	0.00						
Unidentified									0.21	0.00	0.00						
Hydrogen cyanide	HCN									0.94	2.46	2.89	2.63	3.75	6.10	9.68	10.83
2-Propenenitrile	C3H3N									0.48	0.53	0.63	0.51	0.70	0.30		
Ethylbenzene	C8H10									0.78	0.00						
Ethenylbenzene	C8H8									0.40	1.17	1.19	0.94	0.40			
Benzonitrile	C7H5N									0.23	1.43	2.73	4.49	5.21	5.25	2.07	0.48
1-Ethenyl-2-methylbenzene	C9H10									0.65	1.24	1.11	0.52				
Diethylbenzene	C10H14									0.57	0.00						

TABLE 10. (CONTINUED)

Compound	Molecular Formula	Temperature (°C) 300	400	400	500	525	550	600	650	700	750	800	850	900	950	1000
Diethenylbenzene	C10H10								0.30	0.39	0.38					
Methyl-butenyl benzene	C11H14								0.64	0.59						
Ethyl-1H-Indole	C10H12N								1.22	0.00						
Quinoline or isomer	C9H7N								0.88	1.54	2.06	3.12				
Methylbenzonitrile	C8H7N								0.50	0.98	0.66	0.40	0.47			
4-(Dimethylethyl)phenyl-naphthalene	C20H21								2.48	6.31	5.45	1.92				
Dibenzofuran	C12H8O								0.52	0.00						
Unidentified									0.48	0.52	0.64	0.26	0.18	0.26		
Unidentified									0.72	1.66	2.42	0.28				
Unidentified									0.77	0.00						
Unidentified									1.28	0.70						
Unidentified									1.05	0.00						
24.00 - Unidentified										1.14	2.11	1.48	1.31			
Benzene	C6H6									1.63	2.26	3.40	4.30	7.13	8.86	5.72
Toluene	C7H8									0.63	0.72	0.94	0.71	0.57	0.93	0.32
Methyl-benzonitrile	C8H7N									0.66	0.93	0.77	0.52	0.20		
Quinoline or isomer	C9H7N									0.44	0.53	0.29	2.04	1.29		
Naphthalene	C10H8									0.65	1.05	1.72	1.92	3.27	4.12	2.15
Unidentified										0.12						
Unidentified										0.18						
Unidentified										0.85	1.20					
Unidentified										2.49	1.23	0.51				
Unidentified											0.33					
Unidentified											0.57					
Unidentified											0.39	0.18				
Quinoline or isomer	C9H7N											0.60	0.55			
Ethynylbenzene	C8H6												0.52	0.33		
Biphenylene or acenaphthalene	C12H10												0.39	0.78	1.59	1.07
Naphthalene carbonitrile or isocyanonaphth	C11H7N												0.95	0.70	0.51	0.43
Unidentified														0.63	0.77	
Phenanthrene or 9-methylene-9H-fluorene	C14H10														0.76	0.74
Fluoranthene or isomer	C16H10														0.72	0.70
Fluoranthene or isomer	C16H10															0.57

TABLE 11. QUALITATIVE DATA OF PHORATE OXIDATION PRODUCTS

Compound	Temperature (°C) 200	250	275
Phorate	XXXX[1-4]	XXX	
Ethanol	XXXX		
Ethanthiol	XXXX		
Methanethiol	XXX		
1,2,4-Trithiolane	XXX		
1,1-Thio-bis-ethane	XXX		
1,1'-[Methylenebis(thio)]-bis-ethane	XXX		
1,3,5-Trithiane	XXX		
O,O-Diethyl-S-pentenyl-phosphorodithioc acid	XXXX	XXXX	
O,O-Diethyl-S-alkyl-phosphorodithioac acid isomers	XXXX	XXXX	
1,2,4-Trithiolane	XXX		
Ethyl-thio-acetic acid	XXX		
Diethyldisulfide	XXX		
2,2'-Dithio-bis-ethanol	XXX		
Ethyl-(1-methyl-propyl)-disulfide	XXX		
Sulfur dioxide	X	XX	XX
Carbon monoxide	X	XX	XX
Carbon dioxide	X	XX	XX
Sulfuric acid	<X	X	XX
Phosphine		X	X
Unidentified[5]	XXXX	XXX	

1) 'X' depicts an area count response such that 10,000 < X < 100,000
2) 'XX' depicts an area count response such that 100,000 < X < 1,000,000
3) 'XXX' depicts an area count response such that 1,000,000 < X <10,000,000
4) 'XXXX' depicts an area count response such that 10,000,000 < X < 100,000,000
5) The value for 'Unidentified' is a summation of the areas of all unidentified peaks at that temperature

TABLE 12. QUALITATIVE DATA OF PHORATE PYROLYSIS PRODUCTS

	Temperature (°C)						
Compound	200	250	300	325	350	375	400
Phorate	XXX[1-4]		XXX	XXXX	XXXX	XXX	XXX
Ethanthiol	XX		XXXX	XX	XXXXX		XX
1,1'-[Methylenebis(thio)]-bis-ethane		X	XX	XXX		XX	
Carbon dioxide	X	X	X	X	XX	XX	XX
Ethanol			XXXX	XXXX			
Thiirane			XX				
Methyl-thio-ethane			XXX				
Tetramethylphosphine			XXX				
1,1-Thio-bis-ethane			XXX				
Ethyldisulfide			XX				
Dimethyldisulfide			XX				
Heptyl-thiophene			XXX	XX			
1,3,5-Trithiane			XXX		X		
Sulfur dioxide						X	XX
Carbon disulfide							XX
Unidentified[5]	XXX	XXX	XX	XX			

1) 'X' depicts an area count response such that 10,000 < X < 100,000
2) 'XX' depicts an area count response such that 100,000 < X < 1,000,000
3) 'XXX' depicts an area count response such that 1,000,000 < X < 10,000,000
4) 'XXXX' depicts an area count response such that 10,000,000 < X < 100,000,000
5) The value for 'Unidentified' is a summation of the areas of all unidentified peaks at that temperature

TABLE 13. QUALITATIVE DATA OF POLYETHYLENE BAG OXIDATION PRODUCTS

	Temperature (°C)					
Compound	300	400	500	600	700	750
Acetone	XXX[1-4]	XXX	XXX	XX		
2-Oxopropanal	X	XXX				
3,5-Dipropyl-1,2,4-trioxolane	XX		XX	XX		
Dihydro-2-methyl- 3(2H)furanone	XX		XX	XX		
1-Acetyloxy-2-butanone	X					
Pentenal		X				
Hexenal		XX	XXX	XX	XX	
Dihydro-2(3H)-furanone	XX	XX	XXX	XX		
Dihydro-2,5-furan-dione		XX				
C6 Alkyl-cyclohex-anone	XX	XX				
C7 Alkyl ketone	XX	XXX				
6-Methyl-octadecane	XX	XX				
Hexadecane	XX		XX	XX		
6-Methyl-octadecanal	XX		XX			
Carbon dioxide	XXX	XXX	XXX	XXX	XXX	XXX
Carbon monoxide	XX	XX	XX	XX	XXX	XXX
2,5-Furandione		XX	XX	XX		
Butanedial		XXX	XX	XX		
Benzene					XXX	
Unidentified[5]	XXXX	XXXX	XXXX	XXX		

1) 'X' depicts an area count response such that $10,000 < X < 100,000$
2) 'XX' depicts an area count response such that $100,000 < X < 1,000,000$
3) 'XXX' depicts an area count response such that $1,000,000 < X < 10,000,000$
4) 'XXXX' depicts an area count response such that $10,000,000 < X < 100,000,000$
5) The value for 'Unidentified' is a summation of the areas of all unidentified peaks at that temperature

SECTION 6

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APPENDIX 1

PESTICIDE THERMAL STABILITY DATA SHEET

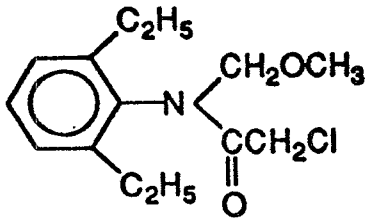
ALOCHLOR
(LASSO-II HERBICIDE)

Empirical Formula: $C_{14}H_{20}ClNO_2$

Molecular Weight: 270 g/mol

IUPAC Name: 2-Chloro-2',6'-diethyl-N-(methoxy-methyl)-acetanilide

Structure:



Data Source	T99 (2)(°C)	Comment
1. Pure compound (Phi = 0.05)	525	No evidence of POHC reformation.
2. Pure compound (Phi = 10)	620	No evidence of POHC reformation.
Evaluation:		Only apparent low energy unimolecular decomposition pathway is C-N fission.
	677	1. C-N fission, rough estimates of rate parameters yield log A = 16.0 1/s and Ea = 68 kcal/mol. Ea based on $C_6H_5CH_2$-$NHCH_3$ bond strength of 68.7 kcal/mol.
		If radical chains are present, H abstraction from two ethyl groups may also contribute to destruction.
Recommendation:		C-N fission (forming resonance-stabilized intermediate) and H abstraction appear to be the rate-controlling decomposition channels. 90°C difference in observed and unimolecular T99 prediction indicates that significant radical chains contribute to destruction.
Ranking:	620	Data Source No. 2.

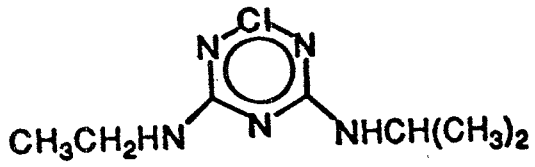
ATRAZINE
(Aatrex Herbicide)

Empirical Formula: $C_8H_{14}ClN_5$

Molecular Weight: 216 g/mol

IUPAC Name: 2-Chloro-4-ethylamino-6-isopropylamino-5-triazine

Structure:



Data Source	T99 (2)(°C)	Comment
1. Pure compound (Phi = 0.05)	475	No evidence of POHC reformation.
2. Pure compound (Phi = 10)	510	No evidence of POHC reformation.
Evaluation:		Two C-N fission channels within aliphatic side chain are dominant initiation pathway:
	755	Rough estimates of rate parameters yield log A = 16.3 1/s and Ea ≥75 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-$NHCH_3$ of 68.7±1 kcal/mol. Since C-N fission for this compound does not form resonance-stabilized radical, Ea must be substantially larger than 69 kcal/mol.
		If radical chains are present, H abstraction from methyl and ethyl groups may also contribute to destruction.
Recommendation:		Theoretical assessment indicates that C-N fission and H abstraction should dominant destruction. 245°C difference in observed and predicted unimolecular T99 suggests that rupture of six-member nitrogen-substituted ring may be contributing to decay. Must analyze reaction products.
Ranking:	510	Data Source No. 2.

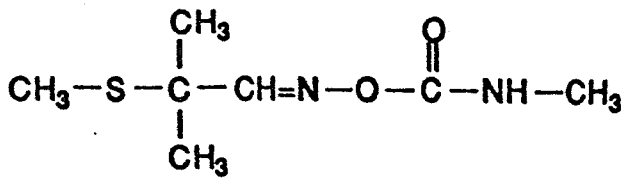
ALDICARB
(Temik Insecticide)

Empirical Formula: $C_7H_{14}N_2O_2S$

Molecular Weight: 190 g/mol

IUPAC Name: 2-Methyl-2-(methylthio)-propionaldehyde-o-(methylcarbamoyl)-oxime

Structure:

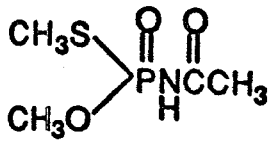


Data Source	T 99 (2)(°C)	Comment
1. Thermal Stability Ranking	510	Based on C-S bond energy estimate of 59 kcal/mol and FY 90 Status Report estimated Arrhenius parameters of log A = 16.0 1/s and Ea = 56 kcal/mol. This is now believed to be in error.
2. Pure compound (Phi - 0.05)	<200	No evidence of POHC reformation.
3. Pure compound (Phi = 10)	<200	No evidence of POHC reformation.
Evaluation:		There are at least two low energy unimolecular decomposition pathways: S-C fission and C-N fission. For this compound, there are 2 C-S routes and 1 C-N route.
	775	1. C-N fission. Rough estimates of rate parameters yield log A = 16.0 1/s and Ea ≥75 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-$NHCH_3$ of 68.7±1 kcal/mol. Since C-N fission for this compound does not form resonance-stabilized radical, Ea must be substantially larger than 69 kcal/mol.
	673	2. C-S fission. D°(C_2H_5-S) = 70.5 kcal/mol. Rough estimates of Arrhenius parameters yield log A = 16.3 1/s and Ea = 69 kcal/mol.
		If radical chains are present, H abstraction from methyl groups may also contribute to destruction.
Recommendation:		C-S fission, C-N fission, and H abstraction may contribute to complex decomposition mechanism. Large descrepancy between observed and predicted unimolecular T99 suggests additional low-energy reaction channels are occurring. Must analyze reaction products.
Ranking:	<200	Data Source No. 3.

ACEPHATE
(Orthene 75 WP Insecticide)

Empirical Formula:	$C_4H_{10}NO_3PS$
Molecular Weight:	183 g/mol
IUPAC Name	o,s-Dimethyl-acetyl-phosphoramiothioate

Structure:



Data Source	T_{99} (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Only apparent low-energy decomposition channel is C-S fission. P-S bond may also be weak.
	691	C-S fission. $D°(C_2H_5\text{-}S) = 70.5$ kcal/mol. Rough estimates of Arrhenius parameters yield log A = 16.0 1/s and Ea = 69 kcal/mol.
		There is no available information to estimate the strength of the P-S bond.
		If radical chains are present, H abstraction from methyl and methoxy groups may contribute to destruction.
Recommendation:		C-S fission, C-N fission, and H abstraction may contribute to complex decomposition mechanism. Estimate of ranking is more uncertain compared to the other insecticides and herbicides evaluated.
Ranking:	600	Theoretical estimate.

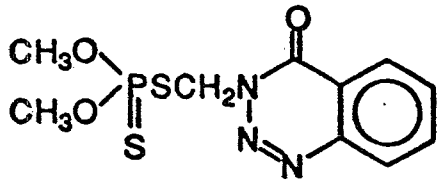
AZINPHOS METHYL
(Guthion WP Insecticide)

Empirical Formula: $C_{10}H_{12}N_3O_3PS_2$

Molecular Weight: 317 g/mol

IUPAC Name: o,o-Dimethylphosphorodithioate-s-ester-3-(mercaptomethyl)-1,2,3-benzotriazin-4(3H)-one

Structure:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Low energy channels dominated by C-S fission. P-S bond may also be weak.
	551	C-S fission, rough estimates of rate parameters yield log A = 16.0 1/s and Ea = 59 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-SCH_3 of 59.4±2 kcal/mol.
		There is no available data to estimate strength of P-S bond.
		If radical chains are present, H abstraction from methoxy group may also contribute to destruction.
Recommendation:		C-S fission (forming resonance-stabilized intermediate) and H abstraction may be rate-controlling decomposition channels.
Ranking:	460	Theoretical estimate.

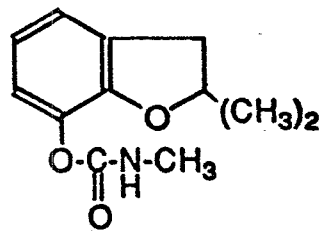
CARBONFURAN
(Furadan Insecticide)

Empirical Formula: $C_{12}H_{15}NO_3$

Molecular Weight: 221 g/mol

IUPAC Name: 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl-methylcarbamate

Structure:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		There are at least two low energy unimolecular decomposition pathways: C-O fission and ring opening in furan (cleavage of C-O bond).
	652	1. C-O fission, rough estimates of rate parameters yield log A = 16.9 1/s and Ea ≥ 70 kcal/mol. Ea based on bond strength of C_6H_5O-C_2H_5 of 63 kcal/mol. Since C-O fission for this compound does not form resonance-stabilized radical, Ea must be substantially larger than 63 kcal/mol. There is no available data to estimate rate parameters for ring opening. If radical chains are present, H abstraction from methyl groups may also contribute to destruction.
Recommendation:		C-O fission and H abstraction may be rate-controlling decomposition channels. Effect of furan ring opening not considered.
Ranking:	560	Theoretical estimate.

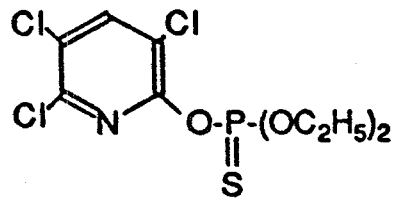
CHLORPRIFOS
(Lorsban Insecticide)

Empirical Formula: $C_9H_{11}Cl_3NO_3PS$

Molecular Weight: 351 g/mol

IUPAC Name: o,o-Diethyl-o-(3,5,6-trichloro-2-pyridyl)-phosphorothioate

Structure:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Low energy channels dominated by six-center elimination of ethylene (two channels)
	570	Rough estimate of Arrhenius parameters yield log A = 12.8 1/s and Ea = 48 kcal/mol. These rate parameters are based on measurement of six-center ethylene elimination from $CH_3COOC_2H_5$ as given in Table 3.12 of S.W. Benson Thermochemical Kinetics. If radical chains are present, H abstraction from ethoxy group may also contribute to destruction.
Recommendation:		Six-center ethylene elimination is very likely to dominate the destruction of this compound. Small contribution from H abstraction may also contribute.
Ranking:	510	Theoretical estimate.

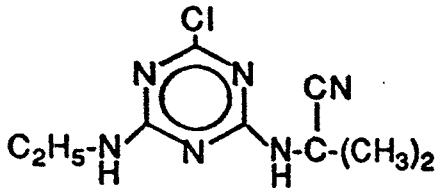
CYANAZINE
(Bladex DF Herbicide/Extrazine II Herbicide)

Empirical Formula: $C_9H_{13}ClN_6$

Molecular Weight: 240 g/mol

IUPAC Name: 2-[[4-Chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylproprionitrile

Structures:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Initiation dominated by C-N fission.
		For the cyanazine compound there are 2 such pathways with the N---C-$(CH_3)_2$ (CN) being slightly faster due to the formation of a resonance-stabilized radical.
	659	Rough estimates of rate parameters yield log A = 16.3 1/s and Ea = 68 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-$NHCH_3$ of 68.7±1 kcal/mol
		If radical chains are present, H abstraction from methyl and ethyl groups may contribute to destruction.
Recommendation:		Decomposition mechanism likely dominated by C-N fission with a small contribution from H abstraction.
Ranking:	500	Should be slightly less stable than ATRAZINE.

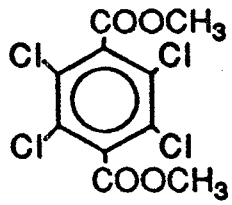
DCPA
(Dacthal W75 Herbicide)

Empirical Formula: $C_{10}H_6Cl_4O_4$

Molecular Weight: 332 g/mol

IUPAC Name: Dimethyl-2,3,5,6-tetrachloroterephthalate

Structure:



Data Source	T_{99} (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Six-center molecular elimination not available as in longer chain phthalates. If radical chains are present, H abstraction from methyl may contribute to destruction.
Recommendation:		Kinetic information on the primary decomposition channels for this compound can only be estimated by analogy with dimethylphthalate (T_{99} = 775°C).
Ranking:	750	Theoretical estimate.

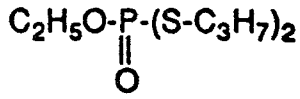
ETHOPROP
(Mocap Granules Insecticide)

Empirical Formula: $C_8H_{19}O_2PS_2$

Molecular Weight: 242 g/mol

IUPAC Name: o-Ethyl-s,s-dipropylphosphorodithioate

Structure:



Data Source	T_{99} (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Six center elimination of ethylene only apparent low-energy decomposition pathway. P-S bond may also be weak.
	591	Rough estimate of Arrhenius parameters yield log A = 12.5 1/s and Ea = 48 kcal/mol. These rate parameters are based on measurement of six-center ethylene elimination from $CH_3COOC_2H_5$ as given in Table 3.12 of S.W. Benson Thermochemical Kinetics. There is no available data to estimate strength of P-S bond. If radical chains are present, H abstraction from n-propyl groups may also contribute to destruction.
Recommendation:		Six-center ethylene elimination is very likely to dominate the destruction of this compound with significant contribution from H abstraction.
Ranking:	530	Theoretical estimate.

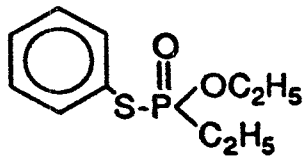
FONOFOS
(Dyfonate Insecticide)

Empirical Formula: $C_{10}H_{15}OPS_2$

Molecular Weight: 246 g/mol

IUPAC Name: o-Ethyl-s-phenyl-ethyl-phosphorodithioate

Structure:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Only apparent low-energy decomposition channel is six-center elimination of ethylene. P-S bond may also be weak.
	591	Rough estimates of Arrhenius parameters for six-center elimination are log A = 12.5 and Ea = 48 kcal/mol. These rate parameters are based on measurement of six-center ethylene elimination from $CH_3COOC_2H_5$ as given in Table 3.12 of S.W. Benson Thermochemical Kinetics.
		There is no available data to estimate strength of P-S bond.
		H abstraction from ethyl group may also contribute to destruction.
Recommendation:		Six-center ethylene elimination and H abstraction may be rate-controlling decomposition channels.
Ranking:	530	Theoretical estimate.

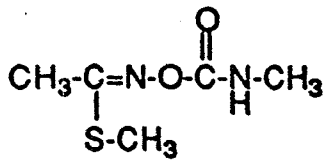
METHOMYL
(Lannate Insecticide)

Empirical Formula: $C_5H_{10}N_2O_2S$

Molecular Weight: 162 g/mol

IUPAC Name: s-Methyl-N-[(methylcarbamoyl)-oxy]-thioacetimidate

Structure:



Data Source	T99 (2)(°C)	Comment
Thermal Stability Ranking FY 90 Status Report	510	Based on C-S bond energy estimate of 59 kcal/mol and estimated Arrhenius parameters of log A = 16.0 1/s and Ea = 56 kcal/mol. This is now believed to be in error.
Evaluation:		C-S fission (two pathways) and C-N fission are believed to be dominant decomposition routes.
	775	1. C-N fission. Rough estimates of rate parameters yield log A = 16.0 1/s and Ea ≥75 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-$NHCH_3$ of 68.7±1 kcal/mol. Since C-N fission for this compound does not form resonance-stabilized radical, Ea must be substantially larger than 69 kcal/mol.
	673	2. C-S fission. D°(C_2H_5-S) = 70.5 kcal/mol. Rough estimates of Arrhenius parameters yield log A = 16.3 1/s and Ea = 69 kcal/mol.
		If radical chains are present, H abstraction from methyl groups may also contribute to destruction.
Recommendation:		C-S fission, C-N fission, and H abstraction may contribute to complex decomposition mechanism. Expected to be slightly less stable than ALDICARB due to the larger number of extractable H atoms.
Ranking:	<200	Based on experimental data for ALDICARB.

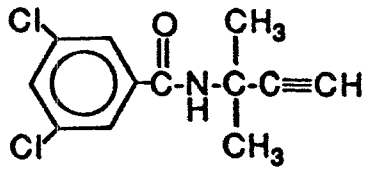
PRONAMIDE
(Kerb WP Herbicide)

Empirical Formula: $C_{12}H_{11}Cl_2NO$

Molecular Weight: 256 g/mol

IUPAC Name: N-(1,1-dimethylpropynyl)-3,5-dichlorobenzamide

Structure:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:		Low energy channels are dominated by C-N fission.
		For this compound, there are 2 C-N routes.
	659	1. C-N fission, rough estimates of rate parameters yield log A = 16.3 1/s and Ea = 68 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-$NHCH_3$ of 68.7 kcal/mol.
		If radical chains are present, H abstraction from methyl groups may also contribute to destruction.
Recommendation:		C-N fission (forming two resonance-stabilized intermediates) and H abstraction may be rate-controlling decomposition channels.
Ranking:	570	Theoretical estimate.

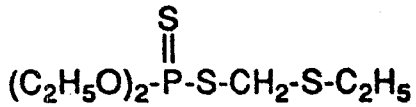
PHORATE
(Thimek Insecticide)

Empirical Formula: $C_7H_{17}O_2PS_3$

Molecular Weight: 260 g/mol

IUPAC Name: O,O-Diethyl-S-(ethylthio)methyl phosphorodithioate

Structure:



Data Source	T_{99} (2)(°C)	Comment
1. Pure compound (Phi = 0.05)	<400	No evidence of POHC reformation.
2. Pure compound (Phi = 10)	<400	No evidence of POHC reformation.

Evaluation:

570 — Possible six-center molecular elimination similar to that observed for esters. Rough estimates of Arrhenius parameters for the two degenerate channels yield log A = 12.8 1/s and Ea = 48 kcal/mol. These rate parameters are based on measurement of six-center ethylene elimination from $CH_3COOC_2H_5$ as given in Table 3.12 of S.W. Benson "Thermochemical Kinetics."

Other low energy channels may include C-S fission (three channels) and P-S fission.

645 — D° (C_2H_5-S) = 70.5 kcal/mol. Rough estimates of Arrhenius parameters yield log A = 16.6 1/s and Ea = 69 kcal/mol.

There is no available information to estimate the strength of the P-S bond.

If radical chains are present, H abstraction from ethyl and ethoxy groups will contribute to destruction.

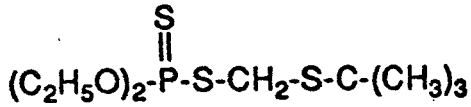
Recommendation: Based on the very limited available data, six-center elimination is believed to be the dominant decomposition channel.

Ranking: 400 — Theoretical estimate. Should be more stable than TERBUFOS due to the greater strength of C-H bonds in methyl versus ethyl groups

TERBUFOS
(Counter Systemmic Insecticide)

Empirical Formula:	$C_9H_{21}O_2PS_3$
Molecular Weight:	288 g/mol
IUPAC Name	s-(((1,1-dimethylethyl)thio)methyl)-o,o-diethyl-phosphorodithioate

Structure:



Data Source	T99 (2)(°C)	Comment
No literature data available	NA	NA
Evaluation:	570	Possible six-center molecular elimination similar to that observed for esters. Rough estimates of Arrhenius parameters for the two degenerate channels yield log A = 12.8 1/s and Ea = 48 kcal/mol. These rate parameters are based on measurement of six-center ethylene elimination from $CH_3COOC_2H_5$ as given in Table 3.12 of S.W. Benson "Thermochemical Kinetics." Other low energy channels may include C-S fission (two channels) and P-S fission.
	645	D° (C_2H_5-S) = 70.5 kcal/mol. Rough estimates of Arrhenius parameters yield log A = 16.6 1/s and Ea = 69 kcal/mol. There is no available information to estimate the strength of the P-S bond. If radical chains are present, H abstraction from methyl and ethoxy groups will contribute to destruction.
Recommendation:		Based on the very limited available data, six-center elimination is believed to be the dominant decomposition channel.
Ranking:	500	Theoretical estimate. Should be of comparable stability compared to PHORATE.

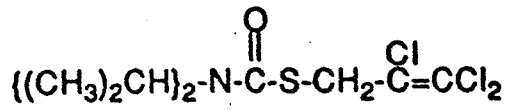
TRIALLATE
(Far-Go Granules Herbicide)

Empirical Formula: $C_{10}H_{16}Cl_3NOS$

Molecular Weight: 305 g/mol

IUPAC Name: s-(2,3,3'-Trichloroallyl)-diisopropyl-thiocarbamate

Structure:



Data Source		T_{99} (2)(°C)	Comment
1. Pure compound in air	516		Data fit to pseudo-first order decay. A = 6.8E8 1/s and Ea = 31 kcal/mol.
Evaluation:			Low-energy channels believed to be dominated by C-N fission, C-S fission, and 4-center HCl elimination.
			For this compound, there are 2 C-N routes, 1 C-S route, and 1 HCl elimination route.
		755	1. C-N fission. Rough estimates of rate parameters yield log A = 16.3 1/s and Ea ≥75 kcal/mol. Ea based on bond strength of $C_6H_5CH_2$-$NHCH_3$ of 68.7±1 kcal/mol. Since C-N fission for this compound does not form resonance-stabilized radical, Ea must be substantially larger than 69 kcal/mol.
		691	2. C-S fission. D°(C_2H_5-S) = 70.5 kcal/mol. Rough estimates of Arrhenius parameters yield log A = 16.0 1/s and Ea = 69 kcal/mol.
		751	3. HCl elimination, using 2,3-dichloropropane by analogy (sp^2 hybridized C), rough estimates of Arrhenius coefficients are log A = 13.8 and Ea = 63 kcal/mol.
			If radical chains are present, H abstraction from methyl groups may also contribute to destruction.
Recommendation:			C-S fission, C-N fission, four-center HCl elimination, and H abstraction may all contribute to this very complex decomposition mechanism.
Ranking:		550	Should be slightly more stable than Data Source No. 1.

APPENDIX 2

RESPONSE FACTORS FOR ANALYTICAL STANDARDS

A complete list of the compounds run as analytical standards in this program is presented below:

	Response Factors	
Compound	Oxidative	Pyrolytic
Carbon Monoxide	50	100
n-Propane	400	600
Acetonitrile	428	350
Carbon Dioxide	50	100
2-Methyl-propane	500	844
Propanenitrile	527	527
Hydrogen Chloride	100	100
n-Butane	450	627
2-Methyl-propenenitrile	300	350
Methane	100	200
2-Methyl-Butane	175	232
Butanenitrile	546	546
Ethane	181	234
n-Pentane	190	230
2-Butenenitrile	554	554
Ethylene	200	240
2-Methyl-pentane	227	227
2-Chloro-propenenitrile	381	381
Acetylene	175	200
n-Hexane	232	232
2-Butenedinitrile	331	331
Sulfur Dioxide	100	350
2,4-Dimethylpentane	230	230
2-Methyl-propanenitrile	538	538
n-Heptane	180	180
Toluene	350	350
n-Octane	180	180
p-Xylene	375	375
n-Propylbenzene	355	355
n-Decane	181	181
n-Butylbenzene	450	450
n-Dodecane	190	190
n-C12	190	190
n-C13	181	181
n-C14	186	186
n-C15	184	184
Alachlor	1000	1000
Atrazine	1200	1200

Compound	Response Factors Oxidative	Response Factors Pyrolytic
Diphenylamine	500	500
Quinoline	500	500
4-Chloro-aniline	500	500
N,N-Dimethylaniline	450	450
Thioacetamide	125	125
Naphthalene	350	350
Aniline	500	500
Benzonitrile	350	350
Benzene	352	352
Acenaphthene	500	500
Acenaphthylene	500	500
Anthracene	500	500
Fluoranthene	450	450
Fluorene	450	450
Phenanthrene	400	400
Pyrene	500	500

APPENDIX 3

MASS BALANCE DATA

TABLE 3.1. ALDICARB OXIDATION

	Weight %		
Temp.(°C)	C	N	S
275	109.1	75.3	140.8
300	93.2	70.1	122.6
350	97.2	72.3	124.6
400	90.1	75.9	115.9
450	114.0	105.1	127.9
500	99.3	97.3	103.4
550	96.2	91.7	114.1
600	103.8	124.9	112.6
650	96.0	97.9	131.2

TABLE 3.2. ALDICARB PYROLYSIS

	Weight %		
Temp.(°C)	C	N	S
300	106.1	73.4	140.5
350	82.6	62.0	111.8
400	104.1	73.0	140.4
450	93.9	54.4	118.9
500	123.6	91.7	130.0
550	120.4	101.3	78.3
600	116.7	105.7	65.4
650	93.5	93.2	74.9
700	94.9	97.6	106.9
750	99.5	106.7	126.7
800	96.0	97.4	132.0
850	103.0	93.9	151.0
900	106.9	84.4	93.3
950	94.6	104.9	106.0
1000	115.7	92.7	109.2

TABLE 3.3. ATRAZINE OXIDATION

Temp.(°C)	Weight %		
	C	N	Cl
275	100.9	100.9	100.9
300	109.9	109.9	100.9
350	104.7	104.6	104.6
400	95.4	94.3	94.5
450	156.9	119.1	93.5
475	89.0	48.4	52.6
500	135.7	79.4	48.0
550	103.4	89.9	112.8
600	107.3	116.0	98.9
650	108.1	153.2	97.4
700	89.1	161.0	99.2
800	42.2	54.6	103.1

TABLE 3.5. ALACHLOR OXIDATION

	Weight %		
Temp.(°C)	C	N	Cl
275	101.2	101.1	101.1
300	98.2	99.1	97.1
350	95.4	97.2	94.2
400	101.6	105.7	91.9
450	79.5	89.0	91.4
500	93.7	101.9	76.0
550	88.9	80.0	97.6
600	84.3	37.2	100.9
650	81.2	141.5	112.8
700	94.4	93.3	106.2

TABLE 3.6. ALACHLOR PYROLYSIS

	Weight %		
Temp.(°C)	C	N	Cl
300	101.2	101.3	101.3
400	96.6	97.8	94.2
450	102.5	105.4	96.4
475	100.3	107.2	88.0
500	122.7	136.6	95.0
525	135.8	138.3	102.3
550	95.0	94.3	69.7
600	91.9	83.2	126.4
650	99.9	81.0	118.7
700	69.3	52.0	100.6
750	80.4	53.2	90.1
800	69.6	51.5	69.4
850	78.9	60.3	78.2
900	70.9	78.8	94.3
950	73.5	102.7	100.7
1000	63.5	109.9	95.3