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Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal Volume 2. Data on 54 Chemicals

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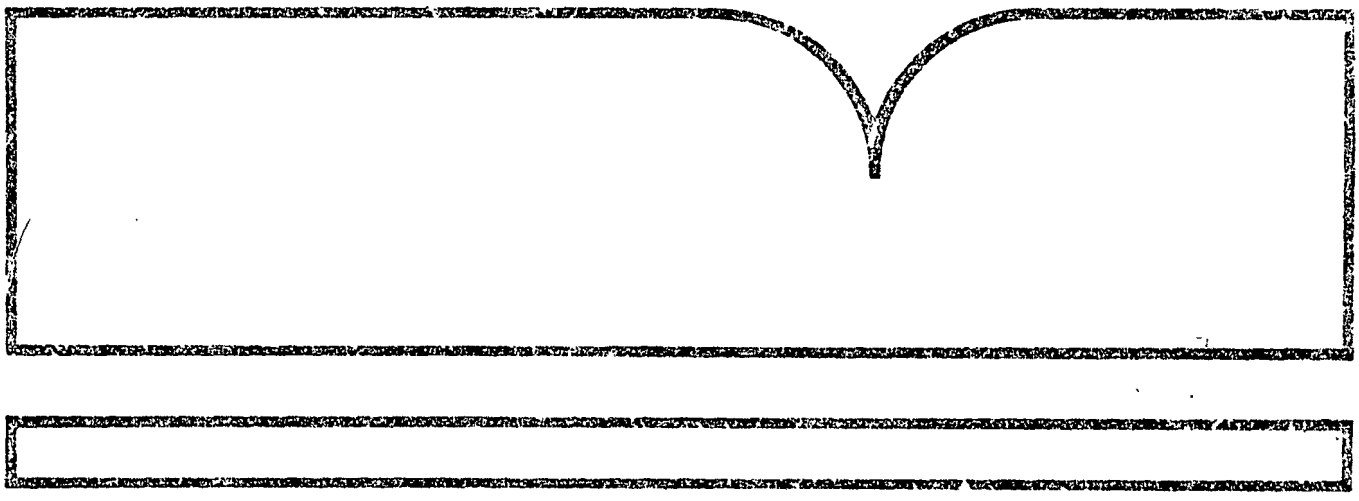

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16. ABSTRACT

To provide input data for mathematical models to estimate potential groundwater contamination from chemicals in land disposal sites, hydrolysis rate constants were determined under carefully controlled conditions. Rate constants are reported for 54 compounds: n-(aminothioxomethyl) acetamide, acetonitrile, 2-acetylaminofluorine, auramine, azaserine, chlorambucil, chordane, chlornaphazine, beta-chlornaphthalene, 2-choloro-1,3-butadiene, 1-(O-chlorophenyl) thiourea, 3-chloropropanenitrile, cyclophosphamide, DDD (p,p' isomer), daunomycin, diallate, dichloroethyl ether, 1,2-dichloropropane, O,O-diethyl-O-pyranzinyl phosphorothioate, diisopropylfluoro phosphate, dimethoate, 2,4-dithiobiuret, ethyl methanesulfonate, ethylene thiourea, ethylene-bis-(dithiocarbamic acid), 2-fluoroacetamide, hexachlorobenzene, hexachloroethane, hexaethyl tetraphosphate, isodrin, lasiocarpine, lindane, malonitrile, melphalan, methomyl, methyl methacrylate, N-methyl-N-nitro-N-nitroso-guanidine, 2-methylaziridine, methylthiouracil, alpha-naphthaylthiourea, N-nitroso-N-ethylurea, n-nitroso-n-methylurethane, octamethylpyrophosphoramide, di-n-octylphthalate, phorate, 1,3-propane sultone, safrole, tetraethyl pyrophosphate, thioacetamide, thiram, toxaphene, O,O,O-triethyl-ester phosphorothioic acid, O,O,S-triethylester phosphorodithioic acid, and tris(2,3-dibromopropyl)phosphate.

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MEASUREMENT OF HYDROLYSIS RATE CONSTANTS FOR EVALUATION OF HAZARDOUS WASTE LAND DISPOSAL: Volume 2. Data on 54 Chemicals

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ABSTRACT

To provide input data for a mathematical model to estimate potential groundwater contamination from chemicals in land disposal sites, hydrolysis rate constants were determined for 31 regulated chemicals under carefully controlled conditions. Hydrolysis rates were measured under sterile conditions at precisely controlled temperatures and at three pH levels (3,7, and 11). Conditions were adjusted to provide sufficiently precise rate constants to meet modeling requirements determined through model sensitivity tests. In addition to close monitoring of temperature and pH, precautions were taken to minimize impact of adventitious processes. Chemical concentrations as a function of incubation time were measured by gas chromatography, liquid chromatography, or ion exchange chromatography. Identities and purities of the chemicals were determined by mass spectrometry supplemented, in some cases, by infrared spectrometry.

Four chemicals (DL-trans-4-chlorostilbene oxide, benzyl chloride, 2,4-dichlorophenoxyacetic acid methyl ester, and lindane) were used as standard reference compounds (SRCs) to ensure reproducibility and control of two parameters, temperature and pH, that affect hydrolysis rates of chemicals in an aqueous environment. The acetate and lindane were used as SRCs in the pH ranges of 8 to 9.5 and 9.5 to 11, respectively. Benzyl chloride and the stilbene oxide were used in conjunction with neutral and acidic hydrolysis rate determinations, respectively. Determinations of the hydrolysis rates of the SRCs were repeated at varying temperatures and pH's over a 15-month period. During the study, the rates for the SRCs were determined on four gas chromatographs and three liquid chromatographs by four chemists. For these determinations the greatest variability from the mean at the 95% confidence limit was ±12% for the acetate. The mean and uncertainty at the 95% confidence level was: stilbene oxide ($17.0 \pm 2.0\ M^{-1}\ min^{-1}$), benzyl chloride [$(7.2 \pm 0.5) \times 10^{-4}\ min^{-1}$], acetate ($699 \pm 77\ M^{-1}\ min^{-1}$), and lindane ($3.3 \pm 0.1\ M^{-1}\ min^{-1}$).

Hydrolysis rate constants are reported for the following 54 compounds:

n-(aminothioxomethyl) acetamide, acetonitrile, 2-acetylaminofluorine, auramine, azaserine, chlorambucil, chlordane, chlornaphazine, beta-chlornaphthalene, 2-chloro-1,3-butadiene, 1-(O-chlorophenyl) thiourea, 3-chloropropanenitrile, cyclophosphamide, DDD (p,p' isomer), daunomycin, diallate, dichloroethyl ether, 1,2-dichloropropane, 0,0-diethyl-O-pyranzinyl phosphorothioate, diisopropylfluoro phosphate, dimethoate, 2,4-dithiobiuret, ethyl methanesulfonate, ethylene thiourea, ethylene-bis-(dithiocarbamic acid), 2-fluoroacetamide, hexachlorobenzene, hexachloroethane, hexaethyl tetraphosphate, isodrin, lasiocarpine, lindane, malononitrile, melphalan, methomyl, methyl methacrylate, N-methyl-N-nitro-N-nitroso-guanidine, 2-methylaziridine, methylthiouracil, alpha-naphthaylthiourea, N-Nitroso-N-ethylurea, n-Nitroso-n-methylurethane, octamethylpyrophosphoramide, di-n-octylphthalate, phorate, 1,3-propane sultone, safrole, tetraethyl pyrophosphate, thioacetamide, thiram, toxaphene, o,o,o-triethyl-ester phosphorothioic Acid, 0,0,S-triethylester phosphorodithioic acid, tris(2,3-dibromopropyl)phosphate.

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FOREWORD

As environmental controls become more expensive and penalties for judgment errors become more severe, environmental management requires more precise assessment tools based on greater knowledge of relevant phenomena. As a part of this Laboratory's research on occurrence, movement, transformation, impact, and control of chemical contaminants, the Measurements Branch determines the occurrence of unsuspected organic pollutants in the aquatic environment and develops and applies techniques to measure physical, chemical, and microbial transformation and equilibrium constants for use in assessment models and for development of property reactivity correlations.

In implementing the land banning provision of the 1984 Hazardous and Solid Waste Amendments to PL 98-616 (RCRA), a mathematical model was developed to estimate potential groundwater contamination from chemicals in land disposal sites. Application of the model requires as input the hydrolysis rate constant(s) for the chemical of concern. This report documents the laboratory measurement of hydrolysis rate constants for 31 compounds regulated under RCRA. Approximately four thousand chemical analyses were required on 35 different organic compounds (including standard reference compounds) to perform the rate constant measurements. Experimental conditions were selected and carefully controlled to provide sufficiently precise rate constants to meet the requirements resulting from model sensitivity tests.

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All compounds except 2-chloro-1, 3-butadiene, ethylene thiourea, hexachlorobenzene, hexachloroethane, and safrole were hydrolyzed to some extent under the varying conditions of pH and temperature employed. Half-lives of hydrolyzable compounds ranged from a few minutes to centuries at pH 7 and 25°C.

This report covers a period from August 1986 to May 1987, and work was completed as of May 1987.

ACKNOWLEDGMENTS

This work was conducted at the Athens Environmental Research Laboratory through the combined efforts of EPA, Technology Applications, Inc. (TAI), and University of Georgia (UGA) personnel. The technical assistance of Miss Sarah Patman (UGA) is gratefully acknowledged. Mr. Alfred Thruston and Dr. Timothy Collette generated the chemical spectral data (Appendices A and B) needed to verify identity and estimate purity. The assistance of Mr. Heinz Kollig in literature searches for hydrolysis data and methods of analysis and review of this report is gratefully acknowledged. The assistance of Dr. Lee Wolfe throughout the project and including review of this report is also gratefully acknowledged. Discussions with Mr. William Donaldson were always fruitful and are so acknowledged. Mrs. Karin Blankenship's effort in typing the draft and subsequent revisions was exemplary.

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SECTION 1

INTRODUCTION

1.1 Purpose

In implementing the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA), EPA's Office of Solid Waste (OSW) will apply a decision rule based on a mathematical model to chemicals under consideration that considers horizontal underground movement of a chemical based on advection, dispersion, sorption, and chemical hydrolysis. Application of the model requires as input the second-order or first-order hydrolysis rate constants for chemicals containing hydrolyzable functional groups. A total of 362 compounds, divided into three groups, are to be regulated initially. This report provides first- and second-order hydrolysis rate constants for those organic compounds in the second group for which satisfactory values were not developed in an earlier evaluation process and describes the laboratory experiments conducted to measure hydrolysis rate constants (1).

1.2 Background

The Hazardous and Solid Waste Amendments of 1984 to PL 98-616 (RCRA) stipulate that land disposal of "hazardous wastes" is prohibited unless the EPA Administrator determines that prohibition of some wastes is not required to protect human health and the environment because those particular wastes are not likely to reach unacceptable levels in groundwater as a result of land disposal. The amendments define hazardous waste as any of 362 specific compounds (either part of or inclusive of Appendix VIII compounds). In compiling this list, major considerations were toxicity of the material and quantity of waste material generated annually.

To provide a practical tool for determining which listed hazardous materials may be disposed of by land disposal and under what conditions, the use of a relatively simple model was suggested that would estimate potential groundwater contamination for each listed chemical. The model considers horizontal movement based on advection, dispersion, sorption, and transformation. Hydrolysis is the only transformation process specifically considered. Although other transformation processes, such as microbial degradation and chemical reduction, may take place, they are not presently included in the model. The model assumes no unsaturated zone for groundwater and assumes saturated groundwater "zones" ranging from 3 meters to 560 meters in depth. The mean depth of those considered is 78.6 meters. Organic carbon contents used in the model will range from 1% to 0.1%. The point at which the groundwater must meet standards may vary but was orignally set at 150 meters horizontally from the point of introduction.

For each chemical considered, the maximum allowable concentration for the receiving groundwater, 150 meters "downstream," is entered into the model, which assumes environmental characteristics for selected subterranian systems. The concentration of leachate leaving the disposal site is computed for various conditions of rainfall, soil type, pH, etc. A computed leachate concentration that would cause unacceptable groundwater conditions is selected by OSW as the

maximum allowable concentration in leachates. A chemical may be disposed of by land only if treatment brings the leachate concentration down to the level selected that would not cause groundwater to exceed the acceptable concentration. The modeling approach applies to landfills, surface impoundments, waste piles, and land treatment operations. Land treatment operations may be addressed in a different manner to allow for reduction in concentrations resulting from the land treatment process.

It is necessary to acquire octanol/water partition coefficients and hydrolysis rate constants for each of the 362 chemicals except for solvents ("fast track" in the list), which will be treated as non-degrading, non-sorbing constituents and chemicals already banned by the State of California (listed as "California"). These two groups comprise 21 and 44 chemicals, respectively. The remainder of the 362 chemicals were separated into 3 groups by OSW: 81 in the "first third," 121 in the "second third," and 95 in the "third third." Rate constant and partition coefficient data are required for these three groups by 7/86, 5/87, and 4/88, respectively. Partition coefficient data are reported in a companion document and have corresponding delivery dates.

Hydrolysis of the organic compounds on the OSW list of chemicals was addressed by a working group of four experts assembled at the Environmental Research Laboratory, Athens, GA, on April 25 and 26, 1985. The experts were chosen for their extensive theoretical and experimental knowledge and experience in the area of chemical reactivity of organic compounds in water. The work group consisted of Dr. N. Lee Wolfe, U.S. Environmental Protection Agency, Athens, GA; Dr. Robert Taft, University of California, Irvine, CA; Dr. Clifford Gunton, University of California, Santa Barbara, CA; and Dr. William Mabey, Kennedy/Jencks Engineers, San Francisco, CA.

The panel addressed only the organic compounds on the list of 362 chemicals provided by OSW. The inorganics included on the list were not addressed. The inorganics will be examined by another group and reported under a separate task. For the organometallic compounds on the list, the panel did not attempt to estimate data, but did provide experimental rate data where available.

The evaluative procedure the panel followed was to divide the compounds into three categories: those that had no hydrolyzable functional groups, those that would hydrolyze with half-lives greater than a year, and those that would hydrolyze with half-lives of less than a year. Hydrolysis rate data were provided for some of the chemicals on the list. The present and previous report was concerned with developing hydrolysis rate data for the remainder.

Of the 81 compounds in the "first third," 54 are either inorganic, contain no hydrolyzable functional group, contain a hydrolyzable functional group that was judged by experts to be non-labile, or have acceptable literature values for hydrolysis reported by Wolfe (1). Acceptable first or second-order hydrolysis rate constants for the remaining 27 compounds in the "first third" is described in "Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal, EPA/600/3-86/043.

The present report covers the 121 "second third" chemicals. Of the 121 compounds, 67 were eliminated for the reasons cited above. Acceptable first or second-order hydrolysis rate constants for the remaining 54 compounds is described in the text of this report.

Table 1 lists the chemical name and Chemical Abstract Number of the 54 "second third" compounds. The CAS number was used as the definitive chemical descriptor when there was any ambiguity in relating the name of the chemical to the structure of the compound. The expert panel did not have time to conduct an extensive search of the literature because of the number of compounds and short time period. Before beginning laboratory measurements, we, therefore, conducted a three-pronged search of the literature. The literature was searched for methods of chemical analysis, laboratory generated hydrolysis values, as well as protocols to follow in laboratory generation of hydrolysis data. The literature searches were conducted either manually or electronically through use of DIALOG, a database management system that yields access to over 200 databases. Compounds with acceptable rate data extracted from the literature are noted in Table 6, the summary table for rate data on the 54 compounds.

Suggested screening protocols and detailed test protocols for hydrolysis of chemicals in water were reported by Mabey et al. (2). Suffet et al. (3) suggested refinements to the above hydrolysis protocols. Neither source documented detailed laboratory methods to apply the suggested protocols; however, the suggested protocols were based on present knowledge of the theory and experimental aspects of hydrolysis and, therefore, provided a good foundation to initiate the laboratory determination of hydrolysis rate constants for the OSW chemicals. The methods used for generation of the reported data evolved after consideration of the two documents, discussions with Dr. Lee Wolfe, Athens ERL, and our experience with the "first third" measurements.

The concept of standard reference compounds (SRC) evolved from discussions with Dr. Wolfe, Mr. William F. Donaldson, and Mr. Heinz Kollig all of Athens ERL. Standard reference compounds are compounds that are used as quality assurance standards and as references in inter-laboratory generation of hydrolysis data. Repetition of rate constant measurement for these compounds over the course of the two reporting periods has established baseline information for evaluating experimental techniques and for all aspects of quality assurance. Four compounds were selected, one each for acid and neutral hydrolysis, and two for basic hydrolysis (Section 3.1).

Each standard reference compound is also amenable to analysis by both gas chromatography and liquid chromatography. Reproduction of the hydrolysis constants of the SRCs at the established concentrations, pHs, and temperatures insured that the experimental conditions for each set of compounds were acceptable and the rate constants for the OSW compounds could be determined with required precision and accuracy. Tables 2 through 5 (Section 5.5.2) contain SRC rate constant data generated during laboratory determinations of rate constants of the OSW compounds. A range of pseudo-first-order hydrolysis rates for all SRCs and second-order rate constants for the acidic and basic reference compound were established from these determinations.

1.3 References for Section 1

1. Wolfe, N. Lee: "Screening of Hydrolytic Reactivity of OSW Chemicals," submitted to Office of Solid Waste and Emergency Response, U.S. EPA, Washington, DC. May 1985.

2. Mill, T., W. R. Mabey, D. C. Bomberger, T. W. Chou, D. G. Hendry, and J. H. Smith. 1982. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-82/022.

3. Suffet, I. H., C. W. Carter, and G. T. Coyle. 1981. Test Protocols for the Environmental Fate and Movement of Toxicants: Proceedings of a Symposium of the Association of Official Analytical Chemists (AOAC), October 21, 1980, Washington, DC, Edited by G. Zweig and M. Beroza, Published January 1981 by the AOAC.

TABLE 1. Chemicals From OSW "Second Third List

CAS Number	Chemical
591-08-2	n-(Aminothioxomethyl)-acetamide
75-05-8	Acetonitrile
53-96-3	2-Acetylaminofluorine
492-90-8	Auramine
115-02-6	Azaserine
305-03-3	Chlorambucil
57-74-9	Chlordane
494-03-1	Chlornaphazine
91-58-7	Beta-Chlornaphthalene
126-99-8	2-Chloro-1,3-butadiene
5344-82-1	1-(O-Chlorophenyl)thiourea
542-76-7	3-Chloropropanenitrile
50-18-0	Cyclophosphamide
72-54-8	DDD (p,p' isomer)
20830-81-3	Daunomycin
2303-16-4	Diallate
111-44-4	Dichloroethyl ether
78-87-5	1,2-Dichloropropane
297-97-2	O,O,-Diethyl-O-pyranzinyl phosphorothioate
55-91-4	Diisopropyl fluorophosphate
60-51-5	Dimethoate
541-53-7	2,4-Dithiobiuret
62-50-5	Ethyl methanesulfonate
96-45-7	Ethylene thiourea
111-54-6	Ethylene-bis-(dithiocarbamic acid)

(TABLE 1. Cont.)

640-19-7	2-Fluoroacetamide
118-74-1	Hexachlorobenzene
67-72-1	Hexachloroethane
757-58-4	Hexaethyl tetraphosphate
465-73-6	Isodrin
303-34-4	Lasiocarpine
58-89-9	Lindane
109-77-3	Malanonitrile
148-82-3	Melphalan
16752-77-5	Methomyl
80-62-6	Methyl methacrylate
70-25-7	N-Methyl-N-nitro-N-nitrosoguanidine
75-55-8	2-Methylaziridine
56-04-2	Methylthiouracil
86-88-4	Alpha-Naphthaylthiourea
759-73-9	N-Nitroso-N-ethylurea
615-53-2	N-Nitroso-N-methylurethane
152-16-9	Octamethylpyrophosphoramide
117-84-0	Di-n-Octylphthalate
298-02-2	Phorate
1120-71-4	1,3-Propane sulfone
94-59-7	Safrole
107-49-3	Tetraethyl pyrophosphate
62-55-5	Thioacetamide
137-26-8	Thiram
8001-35-2	Toxaphene
126-68-1	O,O,S-Triethylester phosphorothioic acid
2524-09-6	O,O,S-Triethylester phosphorodithioic
126-72-7	Tris(2,3-Dibromopropyl) phosphate

SECTION 2

HYDROLYSIS KINETICS

2.1 Hydrolysis Mechanism

Hydrolysis of organic compounds refers to reaction of the compound with water in which bonds are broken and new bonds with HO- and H- are formed. A common example is the reaction of an alkyl halide with the loss of halide ion (-X):

$$RX + HOH \text{ ------} > ROH + HX \text{ (or } H^+, X^-)$$

The rate of the reaction may be promoted by the hydronium ion (H^+, or H_3O^+) or the hydroxyl ion (OH^-). The former is referred to as specific acid catalyis and the latter as specific base catalysis. These two processes together with the neutral water reaction were the only mechanisms considered in this study. This allowed direct measurement of the H_3O^+ or OH^- concentration through accurate determination of solution pH.

Some chemicals show a pH dependent elimination reaction:

$$-\overset{H}{C}-\overset{X}{C}- \xrightarrow[OH^-]{H^+ \text{ or}} C = C + HX$$

In this study only the disappearance of substrate was monitored with no attempts to identify mechanisms.

2.2 Rate Laws

If all processes referred to in Section 2.1 are included where the rate of hydrolysis is given by the equation,

$$-\frac{d[C]}{dt} = k_h[C] = k_A[H^+][C] + k_B[OH^-][C] + k_N'[H_2O][C] \qquad (2.1)$$

where [C] is the concentration of reactant and k_h is the pseudo-first-order rate constant at a specific pH and temperature, k_A and k_B are second- rder rate constants and k_N' the pseudo-first-order rate constant for the acid, base and neutral promoted processes, respectively. The water concentration is essentially not depleted by the reaction and much greater than [C], thus $k_N'[H_2O]$ is a constant (k_N).

Equation 2.1 assures each individual rate process is first order in substrate, thus k_h can be defined as:

$$k_h = k_A[H^+] + k_B[OH^-] + k_N \qquad (2.2)$$

Using the autoprotolysis equilibrium expression

$$K_W = [H^+][OH^-] \qquad (2.3)$$

equation 2.2 may be rewritten as

$$k_h = k_A[H^+] + \frac{k_B K_W}{[H^+]} + k_N \qquad (2.4)$$

Equation 2.4 shows the dependence of k_h on $[H^+]$ and on the relative values of k_A, k_B, and k_N.

As a good approximation, the second-order rate constants for acid hydrolysis and for base hydrolysis can be calculated by dividing the pseudo-first order rate constant obtained at the appropriate pH by the hydronium ion or hydroxyl ion concentration, respectively. The half-life of a chemical at a given pH and temperature can be calculated from equation 2.5, where k_h is the observed rate.

$$t_{1/2} = \frac{0.693}{k_h} \qquad (2.5)$$

Data evaluation methods and calculations are discussed in more detail in Section 5.1.

Excellent discussions of the hydrolysis rate laws are provided by Mabey and Mill (1,2).

2.3 Contributing Factors to Hydrolysis Rates

2.3.1 Temperature

Water and oil baths that precisely held temperature were used when experimentally determining rates of hydrolysis (Section 4.4). This removed the contribution of temperature as a variable during the actual experiments.

2.3.2 pH, Buffer Catalysis

NBS calibration standards were used to calibrate the pH meter before measurements. The pH was usually measured at the temperature of analysis. In regions where only k_A contributes to hydrolysis, K_h will decrease by a factor of 10 for each unit increase in pH. Similarly where only k_B contributes to hydrolysis, K_h will increase by a factor of 10 for each unit increase in pH. k_N is for the pH-independent hydrolysis rate measurement. Buffers (0.005 M) were used to control pH and avoid buffer catalysis (3).

2.3.3 Ionic Strength

Ionic strength, depending on the chemical, can lead either to hydrolysis acceleration or retardation. For this reason, concentrations of buffer solutions

were set as low as possible, yet high enough to maintain constant pH over the course of the hydrolysis determination. The compound concentration was correspondingly set low, usually 10^{-4} M or less.

2.3.4 Sterility

Sterile conditions were maintained for all studies to prevent microbial degradation of the chemicals (Section 4.5).

2.3.5 Sorption

Chemicals analyzed by gas chromatography were extracted from the aqueous layer and glass surfaces with iso-octane. Samples analyzed by liquid chromatography were checked for sorption by emptying the sample container, rinsing the container with acetonitrile, and analyzing the acetonitrile in the same manner as the sample.

2.4 References for Section 2

1. Mabey, W. and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compounds in Water Under Environmental Conditions. J. Phys. Chem. Ref. Data. 7(2): 383-415.

2. Mill, T., W. R. Mabey, D. C. Bomberger, T. W. Chow, D. G. Hendry, and J. H. Smith. 1982. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-82/022.

3. Perdue, E. M. and N. L. Wolfe. 1983. Prediction of Buffer Catalysis in Field and Laboratory Studies of Pollutant Hydrolysis Reactions. Environ. Sci. Technol. 17, 635-642.

SECTION 3

LABORATORY DETERMINATIONS

3.1 Standard Reference Compounds (SRC)

Four compounds were used as standard reference compounds, one each for acid and neutral, and two for base hydrolysis. The SRC hydrolysis rate constants were determined before analysis of samples and interspersed with laboratory determination of hydrolysis rates of the compounds in Table 1. Pertinent information as to concentration, pH, temperature, and instrument for analysis is tabulated in Tables 2 through 5. The rate values for all four SRCs are in good agreement with literature or calculated values.

3.1.1 Acid SRC

DL-trans-4-Chlorostilbene oxide was selected as the SRC for acid hydrolysis studies. Operating conditions and calculated rates are in Table 2. The chlorine was essential for analysis by the electron capture detector.

3.1.2 Neutral SRC

Benzyl chloride was selected as the SRC for neutral hydrolysis conditions, since the rate is known to be independent of pH below 13. Also, the degradation rate at room temperature is fast enough to allow easy sampling. Table 3 tabulates analytical parameters. Of particular interest is the last column of K_1 values extrapolated from three elevated temperatures.

3.1.3 Base SRC

a. Methyl-2,4-dichlorophenoxy acetate (2,4-D methyl ester) served as the base SRC in the pH range 8 - 9.5. Table 4 contains rate values and corresponding analytical parameters. Data are reported as calculated from analytical runs.

b. Lindane, not as sensitive to hydroxide ion catalysis, served as the SRC in the pH range 9.5 to 11. Data are reported in Table 5.

3.2 Rate Studies-OSW Chemicals

A general description of laboratory operations will be given in the remainder of this section. A typical hydrolysis experiment consisted of preparing a spiking solution of the compound of interest, preparing buffer solutions, transferring spiked buffer to individual "rate point tubes" (5-ml Teflon lined, screw cap, or sealed ampules), then monitoring degradation by sacrificing individual tubes and determining percentage of the substrate remaining.

Spiking solutions were prepared by dissolving the substrate in acetonitrile, methanol, or water. The concentration was such that 0.1 ml diluted to 100 ml with buffer gave a substrate concentration that was $1x10^{-5}$M or was 50% of the water solubility or less.

Initial hydrolysis runs were performed at pH 3, 7, and 11. Buffers were prepared at these pHs then measured at the temperature of the hydrolysis run. Each run consisted of five or six tubes. Immediate analysis of one tube established the 100% response peak (T_0). Analysis of a second tube within 3 to 6 hours gave a good estimate of sampling frequency for the remaining tubes.

The initial hydrolysis runs were used to set pH and temperature conditions for subsequent rate determinations. The rate determinations were normally performed in triplicate; however, some compounds required more replicates and some less.

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Table 2. Hydrolysis Data For DL trans-4-chlorostilbene Oxide

Date	pH	Temp., (°C)	Method of Analysis	$X10^3$ K_1[a] (min^{-1})	K_2[b] (M^{-1} min^{-1})	K_2(M^{-1} min^{-1}) (Extrapolated[c])
11-1-85	3.13	28.0	LC	17.4	23.5	15.3
11-6-85	3.10	28.0	LC	14.4	18.2	11.8
11-6-85	3.10	28.0	LC	14.9	18.8	12.2
11-6-85	3.07	28.0	LC	14.3	16.8	10.9
11-6-85	3.07	28.0	GC	14.6	17.1	11.1
11-6-85	3.63	38.2	GC	17.0	72.3	11.5
11-15-86	3.01	28.0	LC	20.8	21.3	13.8
11-15-86	3.01	28.0	LC	23.7	24.2	15.7
11-15-86	3.59	38.2	LC	23.5	91.4	14.6
11-15-86	3.59	38.2	LC	24.5	95.3	15.2
11-15-86	3.01	28.0	LC	21.1	21.6	14.0
3-11-86	3.06	28.0	LC	16.9	19.4	12.6
3-11-86	3.06	28.0	GC	14.3	16.4	10.6
3-11-86	3.06	28.0	LC	16.9	19.4	12.6
3-11-86	3.06	28.0	GC	14.4	16.5	10.7
5-14-86	2.99	23.0	LC	12.9	12.6	16.8
8-13-86	2.95	25.3	LC	19.4	17.3	16.6
8-13-86	2.95	25.3	LC	24.2	21.6	20.6
8-15-86	3.03	24.3	LC	11.1	11.9	13.1
11-18-86	2.89	25.0	LC	29.5	22.9	22.9
11-18-86	2.89	25.0	LC	35.8	27.3	27.8
11-19-86	3.05	25.0	LC	24.4	27.4	27.4
11-19-86	3.05	25.0	LC	22.8	25.6	25.6
11-19-86	3.05	25.0	LC	22.8	25.6	25.6
11-19-86	3.02	25.0	LC	17.4	18.2	18.2
11-19-86	3.02	25.0	LC	16.1	16.8	16.8
11-19-86	3.02	25.0	LC	19.0	19.9	19.9
12-31-86	3.10	25.0	LC	16.9	21.2	21.2
12-31-86	2.96	25.0	LC	18.5	16.9	16.9
1-9-87	3.12	23.0	LC	15.5	20.4	27.4
1-9-87	3.13	23.0	LC	10.1	13.6	18.3
						17.0 ± 5.4[d]

a. Pseudo-first-order rate constant from the slope line when ln % remaining versus time was plotted. Standard deviation of slope was <10% in each case.

b. Second-order rate constant.

c. Extrapolation to 25°C using activation energy of 25.6 kcal/mole.

d. Mean and standard deviation of 31 determinations.

Table 3. Hydrolysis Data For Benzyl Chloride

Date	pH	Temp. (°C)	Method of Analysis	$X10^4 K_1(min^{-1a})$	$X10^4 K_1(min^{-1})$ (Extrapolated[b])
11-26-85	7.00	52.9	LC	203.5	8.8
11-26-85	7.00	52.9	LC	191.0	8.3
11-26-85	7.00	52.9	LC	211.3	9.2
11-26-85	7.00	52.9	LC	216.0	9.4
11-27-85	7.00	28.0	LC	10.4	7.2
11-27-85	7.00	28.0	LC	12.2	8.5
11-27-85	7.00	28.0	LC	11.1	7.7
11-27-85	7.00	28.0	LC	9.8	6.8
11-29-85	7.00	45.0	GC	72.7	7.3
11-29-85	7.00	45.0	LC	72.2	7.2
12-2-85	7.00	36.4	GC	31.9	8.3
12-2-85	7.00	36.4	LC	33.9	8.8
5-21-86	7.00	53.4	GC	140.2	5.8
5-21-86	7.00	53.4	GC	136.5	5.6
7-2-86	7.00	53.5	GC	154.3	6.3
8-19-86	7.00	45.0	GC	65.8	6.6
8-22-86	7.00	42.7	GC	70.0	9.0
8-22-86	7.00	46.0	GC	67.0	6.0
8-22-86	7.00	45.0	GC	55.0	5.5
11-19-86	7.00	45.0	GC	63.9	6.4
11-19-86	7.00	45.0	GC	60.6	6.0
11-21-86	7.00	45.0	GC	69.0	6.9
11-21-86	7.00	45.0	GC	69.0	6.9
11-21-86	7.00	45.0	GC	78.0	7.8
1-9-87	7.00	45.0	GC	66.9	6.7
1-9-87	7.00	45.0	GC	69.4	6.9
1-27-87	7.00	49.0	GC	98.9	6.4
1-27-87	7.00	49.0	GC	98.6	6.4
					7.2 ± 1.1[c]

a. First-order rate from the slope of the line when ln% remaining versus time was plotted. Standard deviation of the slope was <10% in each case.

b. Extrapolated to 25°C using activation energy of 22.5 ± 1.4 kcal/mole.

c. Mean and standard deviation of 26 determinations.

Table 4. Hydrolysis Data For 2,4-DME

Date	pH	Temp. (°C)	Method of Analysis	$X10^4$ K_1[a] (min^{-1})	K_2 (M^{-1} min^{-1})	K_2(M^{-1} min^{-1}) (Extrapolated[a])
10-7-85	9.06	28.0	LC	80.7[b]	560[c]	481
10-7-85	9.06	28.0	GC	70.4	489	420
10-8-85	9.65	28.0	LC	262.0	467	401
10-8-85	9.65	28.0	GC	278.0	495	425
10-9-85	7.11	70.3	LC	114.0	5451	729
10-9-85	7.11	70.3	GC	100.0	4775	638
10-11-85	9.14	28.0	LC	118.0	681	585
10-11-85	9.14	28.0	GC	103.0	593	509
10-11-85	8.00	48.5	LC	103.0	2079	682
10-11-85	8.00	48.5	GC	86.0	1731	567
3-6-86	8.87	25.0	LC	57.1	770	769
3-6-86	8.87	25.0	GC	41.8	563	563
3-6-86	9.10	25.0	LC	95.0	754	754
3-6-86	9.10	25.0	GC	79.0	627	627
5-12-86	9.38	25.0	LC	230.0	958	958
5-12-86	9.45	25.0	LC	249.0	883	883
5-13-86	9.38	25.0	GC	224.0	933	933
5-13-86	9.45	25.0	GC	224.0	794	794
7-2-86	8.75	31.0	LC	91.2	1038	768
7-3-86	8.72	31.0	LC	79.2	966	715
8-14-86	8.81	23.0	LC	29.9	541	599
8-14-86	8.81	23.0	LC	33.0	596	661
8-14-86	8.81	23.0	LC	36.0	650	721
12-31-86	8.74	45.0	GC	340.0	1547	593
12-31-86	8.54	45.0	GC	350.0	2520	966
1-9-87	8.55	45.3	GC	412.0	2847	1077
1-9-87	8.55	45.3	GC	415.0	2867	1084
						699 ± 190[d]

a. Extrapolation to 25°C using activation energy of 9.0 (±0.4) kcal/mole.

b. Pseudo-first-order rate constant from slope of the line when ln% remaining versus time was plotted. Standard deviation of slope was <10% in each case.

c. Second-order rate constant, variation of K_W and hydroxide ion concentration with changing temperature included in calculation.

d. Mean and standard deviation of 27 determinations.

Table 5. Hydrolysis Data For Lindane

Date	pH	Temp. (°C)	Method of Analysis	$X10^3$ K_1[a] (min^{-1})	K_2(M^{-1} min^{-1})	K_2(M^{-1} min^{-1}) (Extrapolated[b])
9-2-86	10.98	46.0	GC	71.5	17.6[c]	3.29
9-3-86	10.98	46.0	GC	78.0	19.2	3.59
9-3-86	11.60	22.8	GC	9.9	2.9	3.56
9-3-86	11.29	37.0	GC	40.2	8.7	3.24
9-4-86	11.08	46.0	GC	83.4	16.3	3.05
11-19-86	10.37	45.0	GC	14.8	15.8	3.19
11-19-86	10.37	45.0	GC	14.6	15.6	3.15
11-19-86	10.37	45.0	GC	14.5	15.4	3.11
12-31-86	10.45	45.0	GC	20.0	7.7	3.57
12-31-86	10.31	45.0	GC	18.4	22.5	4.54
1-8-86	10.71	45.3	GC	36.0	17.2	3.39
1-8-86	10.71	45.3	GC	33.1	15.8	3.12
						3.3 ± 0.2[d]

a. Pseudo-first-order rate constant from slope of the line when ln % remaining versus time was plotted. Standard deviation of slope was <10% in each case.

b. Extrapolation to 25°C using activation energy of 15.1 (±0.5) kcal/mole.

c. Second-order rate constant, variation of K_w and hydroxide ion concentration with changing temperature included in calculation.

d. Mean and standard deviation of 12 determinations.

SECTION 4

EXPERIMENTAL

4.1 Chemicals and Solvents

4.1.1 Source

The EPA repositories at Research Triangle Park, NC, and Las Vegas, NV, were the first choice for chemicals on which hydrolysis rates were measured. Commercial chemical companies were the second sources. The supplier of each chemical is listed on the data sheets in the Section 5.3.

4.1.2 Identity and Purity

Stated purities are listed on the data sheets. The chemicals were analyzed by mass spectrometry for confirmation of the stated identity. The generated mass spectral data are in Appendix A. FT-IR was used to characterize three of the "second third" compounds (Appendix B).

4.1.3 Solvents

Solvents were "distilled in glass," Burdick and Jackson solvents either gas chromatograph or HPLC grade, as required by the method of analysis.

4.2 pH Measurement

An Orion Research EA920 pH meter equipped with an Orion Research Δ810300 Ross combination electrode was used for all pH measurements. National Bureau of Standards (NBS) reference standards were used to calibrate and check the pH meter. The pH meter had a stated accuracy of ±0.02 units. The temperature compensation probe was used for all measurements. The pH was measured at the temperature of the hydrolysis rate measurement and adjusted with base or acid to obtain the desired pH.

4.3 Buffers

Buffer stock solutions were prepared at 0.1 M using sterile water as described above. To prepare pH 3 buffer, 0.1 M potassium hydrogen phthalate was diluted to 0.005 M and final pH adjustment made with 0.1 M HCl. The pH 7 buffer was prepared from 0.1 M potassium dihydrogen phosphate diluted to 0.005 M with final pH adjustment using 0.1 M NaOH. Buffers for pHs 9 and 11 were made by diluting 0.1 M sodium phosphate heptahydrate to 0.005 M with final pH adjustment using 0.1 M NaOH.

Buffer stability was tested initially at 0.001 M. Thus, pH 5 and pH 7 buffers held their respective pH's for the test period. The pH 9 buffer (0.001 M) decreased to pH 8.07 after 24 hours and to pH 7.50 after 96 hours. Buffer at a concentration of 0.005 M remained constant at 9.10 ± 0.03 pH units for 25 days. Containers for the experiment were screw cap test tubes. Autoclaved (CO_2 free) water was used.

4.4 Temperature Control

Forma Scientific refrigerated and heated baths (Model 2095) were used for temperatures in the range of 2 to 70°C (±0.02°C). A Lauda C-20 oil bath with a stated control accuracy of ±0.01°C and a fine control range of ±0.2°C was used for temperatures above 68°C. Temperatures were measured with American Society for Testing and Materials (ASTM) thermometers, calibrated by NBS procedures and NBS certified masters. The thermometers were calibrated in 0.1°C increments.

4.5 Sterile Water

Water used in the experiments was unchlorinated ground water that was first processed through a high capacity reverse osmosis unit and a deionizer unit. This "house" deionized water was further purified by passage through a Barnstead Nanopure II deionizer, 4-Module unit with Pretreatment, High Capacity, and Z-Ultrapure cartridges. Water obtained from this unit had a resistance of greater than 16 meg ohms. This double deionized water was autoclaved for 30 min/liter and allowed to cool before use. The sterile water was stored in a sterile-cotton-plugged container until used. All hydrolysis runs were conducted in screw cap tubes. Data from smear plate counts on agar indicated growth as being less than 1 colony per milliliter through 9 days at 25°C and pH of 5, 7, and 9. Sterility checks on the water were performed intermittently.

Buffer solutions were checked for bacterial growth. Buffer solutions, prepared as described above, were transferred at room temperature to screw cap test tubes. One-half were flame transferred, the other half without flaming. A sample (1 ml) from each tube was plated daily, for nine concurrent days on TGE agar. After a 48-hour incubation, no growth was found. This confirmed sterility. Control checks during hydrolysis runs showed no growth.

4.6 Methods of Analysis

Details of the methods of chemical analysis are listed on the data sheet for each compound. Generally gas chromatography was the first method of choice for four reasons:

1) sensitivity and specificity of detectors

2) solvent extraction stopped hydrolysis and allowed multiple injections over extended periods of time

3) solvent extraction also lessened problems caused by compound sorption to glass

4) direct aqueous injection of water soluble compounds that were not amenable to other methods of analysis

High performance liquid chromatography (HPLC) was used extensively; ion chromatography and the diode array UV-detector were used in the analysis of sodium fluoroacetate and thiourea, respectively. Hydrogen cyanide released by the decomposition of 2-methyllactonitrile was monitored by EPA Method 335.

Linearity of detector response in the concentration range of analysis for each chemical was established to ensure reliable concentration versus time plots.

SECTION 5

DATA ANALYSIS AND PRESENTATION

5.1 Data Compilation Methods

Raw data consisted of time of sampling and percentage substrate remaining. The measured concentration at time zero was considered 100% and was the reference point for the remaining points. The data were processed on a Lotus 1-2-3/IBM PC-XT using a data entry/linear regression program. The raw and calculated data were entered in a notebook. Graphs were made by using personal computers to plot ln (% remaining) vs. time and to calculate statistical values.

Values obtained from the linear regression program include the slope (pseudo-first-order rate constant), Y-intercept, variance, SD of Y-intercept, SD of slope, and the correlation coefficient (r^2).

5.2 Standard Reference Compound Data

All the laboratory data on the SRCs are summarized in Tables 2, 3, 4, and 5. Figures 1, 2, and 3 are representative graphical presentations of hydrolysis data for three SRCs. Figure 4 is an Arrhenius plot for hydrolysis of benzyl chloride at four temperatures. See 5.3.32 for lindane data and illustrative figure. An energy of activation of 22.5 ± 1.4 Kcal/mole for benzyl chloride was calculated from the data associated with Figure 4. An error of 10% in the slope was assumed. Arrhenius plots for the other SRCs yielded the following energies of activation: CSO (25.6 kcal/mole); 2,4-DME (9.0 ± 0.4 kcal/mole) and lindane (15.1 ± 0.5 kcal/mole). The change in the hydrolysis rate constants for benzyl chloride and the methyl ester of 2,4-D after March 1986 illustrates how susceptible rate determinations are to slight changes in the controlled parameters. No plausible explanation has been found for either the increased 2 4-D rate or the decreased benzyl chloride rate.

5.3 Summary Sheets for CSW Chemicals

A summary sheet was prepared for each chemical. The summary sheet contains information pertinent to the analysis of each chemical, and includes source, purity, and analytical method. Also included on the sheet is information on pH, temperature, pseudo-first-order and second-order rate constants, half-lives, and correlation coefficients (r^2). Sample identity was confirmed by mass spectrometry and infrared spectrometry as reported in the Appendices. Where a literature reference for the hydrolysis of a compound was obtained, the summary sheet contains the second-order rate constant if applicable and first-order rate constants at 25°C. For several of the compounds, lab data were generated in this study to fill in gaps in the literature.

Data from all the summary sheets were used to derive the values in Table 6. These values are the calculated rate constants at 25°C. The rate constants were assumed to vary a factor of 10 for each 20°C change in temperature (Ref. 1, Section 1). This corresponds to an activation energy of about 20 kcal/mole. When applicable extrapolated values (25°C) were obtained using activation parameters. A temperature correction was applied to all calculations involving K_w or $[OH^-]$. When statistical tests of the data indicated the hydrolysis was

$K_1 = 1.74 \times 10^{-2}\ min^{-1}$

$T_{1/2} = 39.8$ min.

$R^2 = 0.999$

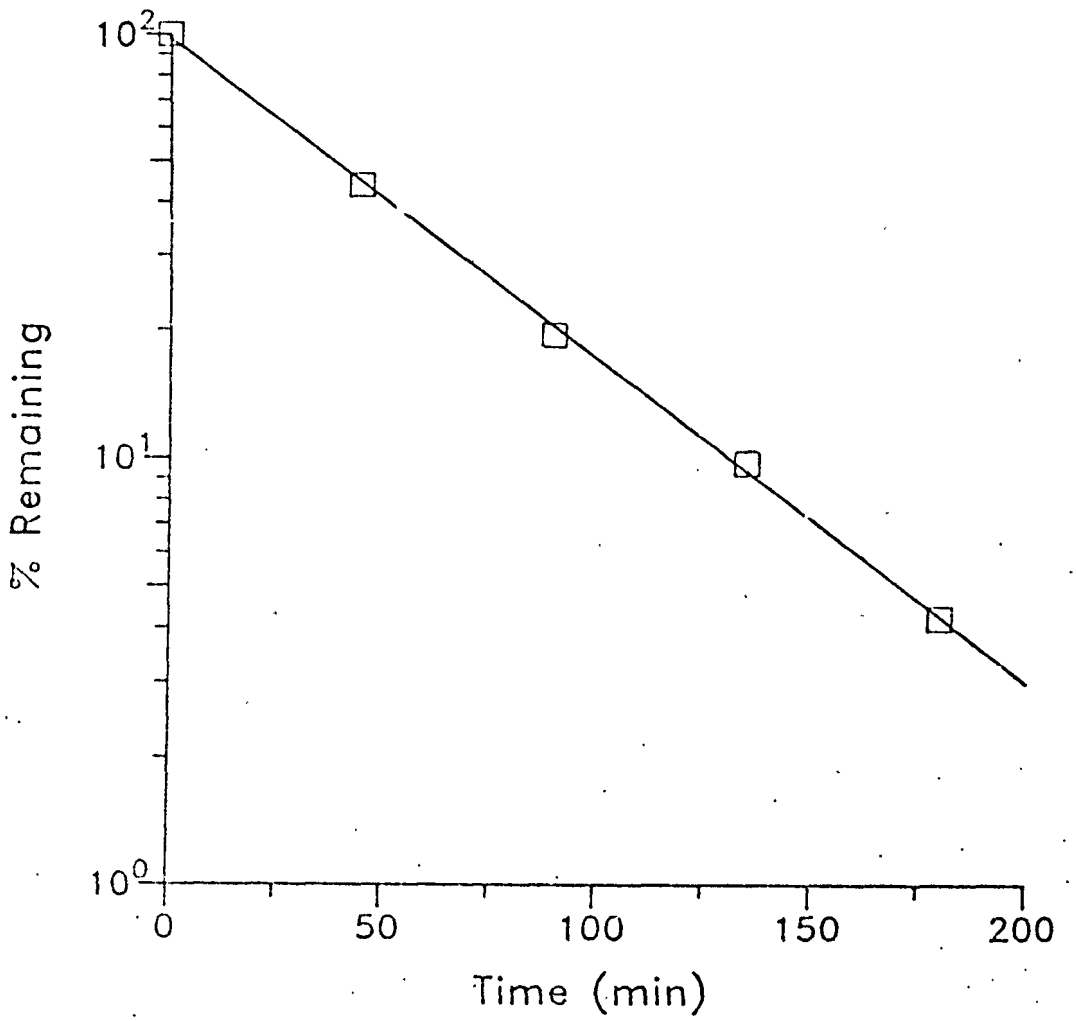

Figure 1. Hydrolysis of DL-trans-4-Chlorostilbene Oxide at 28°C, pH 3.13

$K_1 = 2.04 \times 10^{-2}\ min^{-1}$

$T_{1/2} = 34$ min.

$R^2 = 0.994$

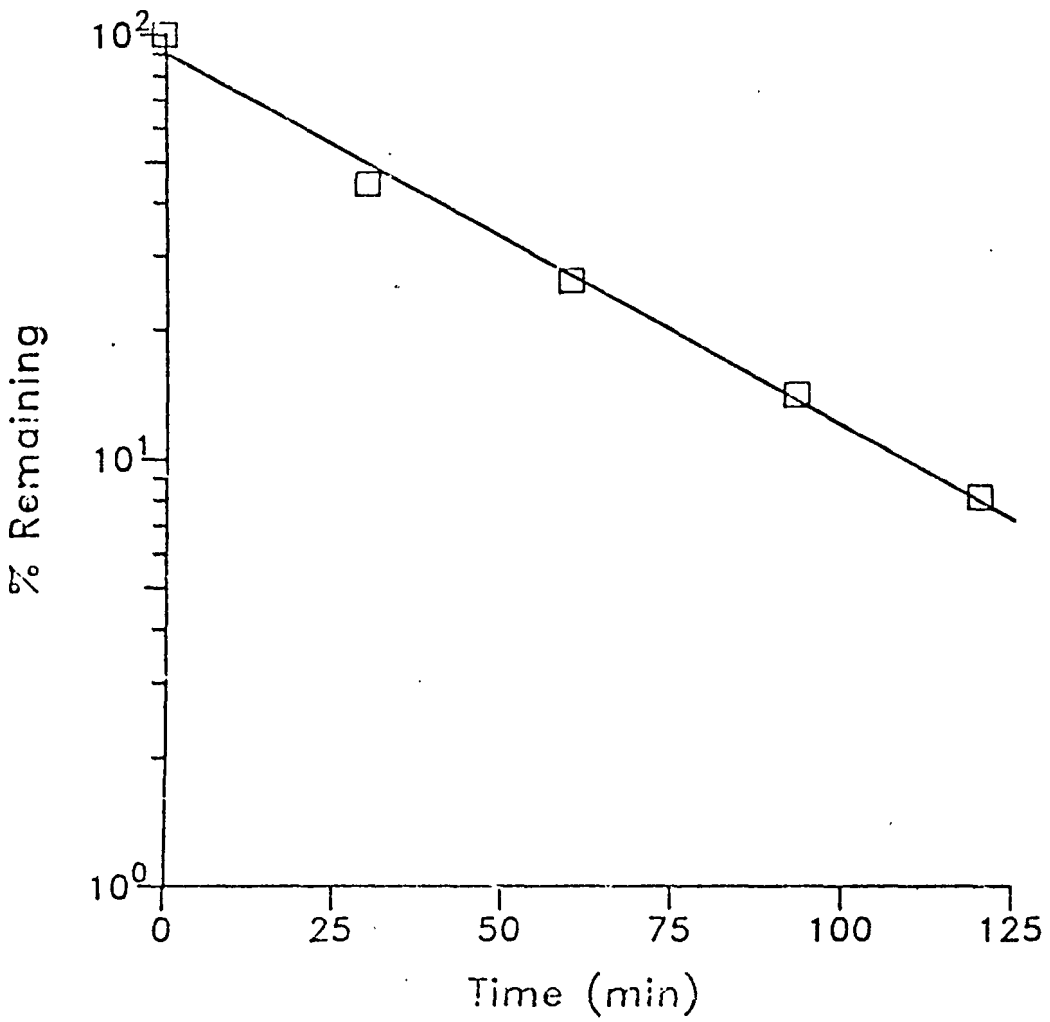

Figure 2. Hydrolysis of Benzyl Chloride at 52.9°C, pH 7.0

$K_1 = 8.07 \times 10^{-3}\ min^{-1}$

$T_{1/2} = 85$ min.

$R^2 = 0.994$

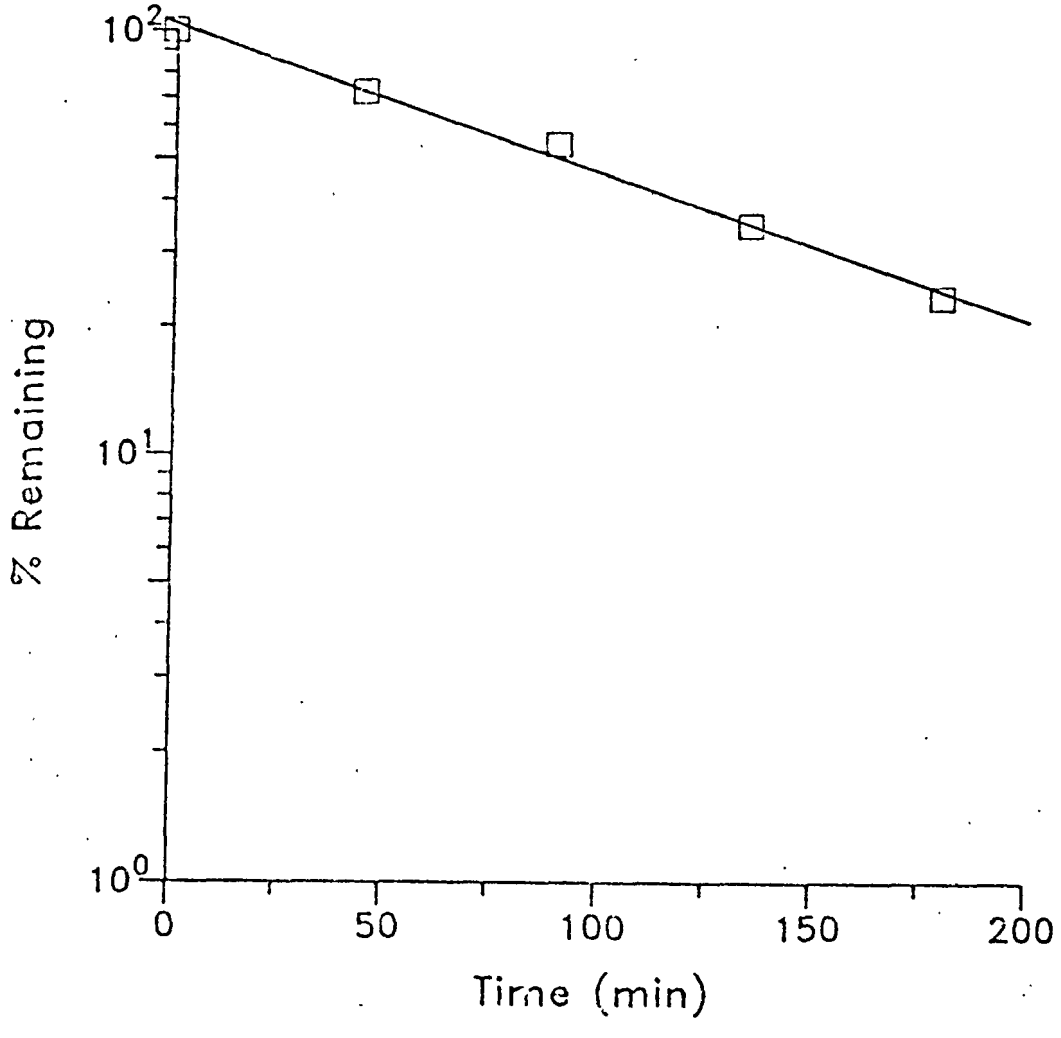

Figure 3. Hydrolysis of Methyl-2,4-Dichlorophenoxy Acetate at 28°C, pH 9.0

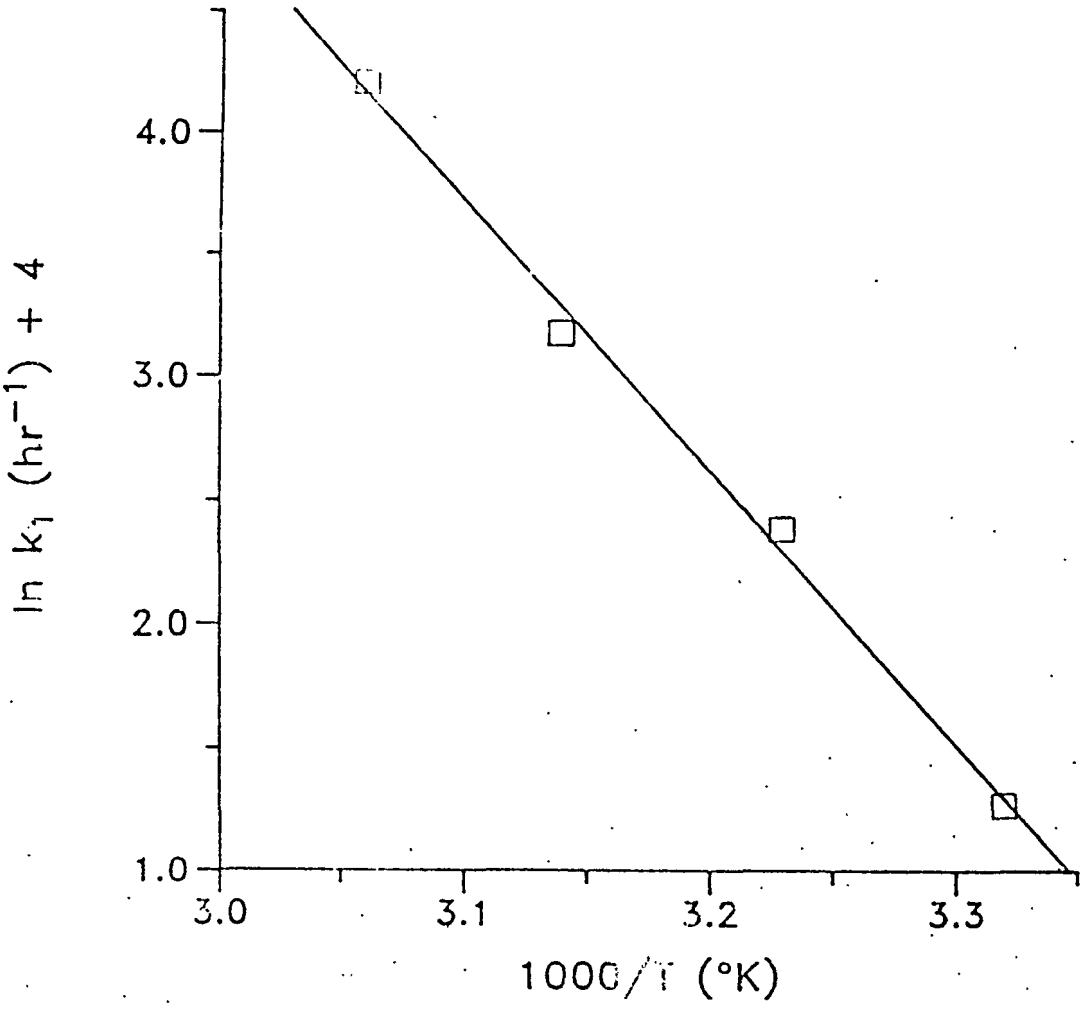

Figure 4. Dependence of Benzyl Chloride Hydrolysis on Temperature

TABLE 6. HYDROLYSIS RATE CONSTANTS AND HALF-LIVES AT 25°C

LABORATORY DETERMINED RATE DATA

CAS Number	Compound	Rate Constants			Calculated Half-Life at pH 7
		ACID M^{-1} hr^{-1}	Neutral hr^{-1}	Base M^{-1} hr^{-1}	
591-08-2	n-(Aminothioxomethyl)-acetamide		$(1.7 \pm 0.2) \times 10^{-5}$	1.59 ± 0.09	4.6 yr
75-05-8	Acetonitrile[a]			5.8×10^{-3}	>150,000 yr
53-96-3	2-Acetylaminofluorine		2.3×10^{-6}	6×10^{-3}	34 yr
492-80-8	Auramine[a]	5.5	3.9×10^{-4}		74 d
115-02-6	Azaserine	328 ± 20	$(2.6 \pm 0.4) \times 10^{-4}$	6.8 ± 0.7	99 d
305-03-3	Chlorambucil[a]		0.4		1.7 hr
57-74-9	Chlordane (cis isomer)			4.3×10^{-3}	>197,000 yr
494-03-1	Chloronaphazine[a]		3.2×10^{-3}		216 hr
91-58-7	Beta-Chlornaphthalene		$(9.5 \pm 2.8) \times 10^{-6}$		8.3 yr
126-99-8	2-Chloro-1,3-butadiene[a]	Polymerizes in absence of inhibitors (no hydrolysis)			
5344-82-1	1-(O-Chlorophenyl)thiourea		$(9.8 \pm 3.0) \times 10^{-7}$	0.14 ± 0.03	81 yr
542-76-7	3-Chloropropanenitrile		$(1.3 \pm 0.1) \times 10^{-4}$	$12,071 \pm 1,960$	22 d
50-18-0	Cyclophosphamide[a]		7.1×10^{-4}		41 d
72-54-8	DDD (p,p' isomer)		$(2.8 \pm 0.9) \times 10^{-6}$	5.2	28 yr

Table 6. cont.

LABORATORY DETERMINED RATE DATA

CAS Number	Compound	Rate Constants ACID M^{-1} hr^{-1}	Rate Constants Neutral hr^{-1}	Rate Constants Base M^{-1} hr^{-1}	Calculated Half-Life at pH 7
20830-81-3	Daunomycin		$(9.7 \pm 0.5) \times 10^{-5}$	10	298 d
2303-16-4	Dialiate		$(1.2 \pm 0.7) \times 10^{-5}$	0.9 ± 0.4	6.6 yr
111-44-4	Dichloroethyl ether[a]		3.2×10^{-2}		22 hr
78-87-5	1,2-Dichloropropane		$(5.0 \pm 0.2) \times 10^{-6}$	4.3×10^{-4}	15.8 yr
297-97-2	O,O-Diethyl-O-pyranzinyl phosphorothioate		$(1.0 \pm 0.06) \times 10^{-3}$	7.3 ± 0.7	29 d
55-91-4	Diisopropyl fluorophosphate[a]	3.8	7.2×10^{-3}	28	96 hr
60-51-5	Dimethoate[a]		1.7×10^{-4}	756	118 hr
541-53-7	2,4-Dithiobiuret		$(7.1 \pm 1.3) \times 10^{-3}$		98 hr
62-50-0	Ethyl methanesulfonate[a]		1.5×10^{-2}		46 hr
96-45-7	Ethylene thiourea	Zero hydrolysis observed after 90 days at 90°C and pH (3, 7, 9)			
111-54-6	Ethylene-Bis-(Dithiocarbamic Acid) [as in disodium salt, Nabam]	848	0.01		69 hr
640-19-7	2-Fluoroacetamide		$(3.3 \pm 0.3) \times 10^{-5}$		2.4 yr
118-74-1	Hexachlorobenzene	Zero hydrolysis observed after 13 days at 85°C and pH (3, 7, 11)			
67-72-1	Hexachloroethane	Zero hydrolysis observed after 11 days at 85°C and pH (3, 7, 11)			

Table 6. cont.

LABORATORY DETERMINED RATE DATA

CAS Number	Compound	Rate Constants ACID M^{-1} hr^{-1}	Rate Constants Neutral hr^{-1}	Rate Constants Base M^{-1} hr^{-1}	Calculated Half-Life at pH 7
757-58-4	Hexaethyl tetraphosphate[a]		9.3×10^{-2}		7.5 hr
465-73-6	Isodrin		1.7×10^{-6}		46 yr
303-34-4	Lasiocarpine		$(4.9 \pm 0.1) \times 10^{-5}$	9.8 ± 0.1	1.6 yr
58-89-9	Lindane		$(1.2 \pm 0.2) \times 10^{-4}$	198 ± 6	206 d
109-77-3	Malononitrile		$(1.35 \pm 0.42) \times 10^{-3}$	806 ± 45	20.2 d
148-82-3	Melphalan[a]		0.15		4.6 hr
16752-77-5	Methomyl[a]		8.9×10^{-5}	210	262 d
80-62-6	Methyl methacrylate			200 ± 47	3.9 yr
70-25-7	N-Methyl-N-nitro-N-nitroso-guanidine[a]	4.9	2.7×10^{-2}	9.5×10^{4}	19 hr
75-55-8	2-Methylaziridine[a]	4.0×10^{-3}	8.0×10^{-3}		87 hr
56-84-2	Methylthiouracil		$(9.7 \pm 2.7) \times 10^{-6}$		8.2 yr
86-88-4	Alpha-Naphthaylthiourea		$(8.0 \pm 2.4) \times 10^{-5}$	9.9×10^{-2}	361 d
759-73-9	N-Nitroso-N-ethylurea[a]	63	0.19	5.3×10^{6}	0.96 hr
615-53-2	N-Nitroso-N-methylurethane[a]	9.5	2.9×10^{-2}	2.9×10^{3}	24 hr

Table 6. cont.

LABORATORY DETERMINED RATE DATA

CAS Number	Compound	Rate Constants ACID M^{-1} hr^{-1}	Rate Constants Neutral hr^{-1}	Rate Constants Base M^{-1} hr^{-1}	Calculated Half-Life at pH 7
152-16-9	Octamethylpyrophosphoramide[a]	0.23 ± 0.03		1×10^{-11}	3,400 yr
117-84-0	Di-n-Octylphthalate[a]			7.4	107 yr
298-02-2	Phorate[a]		7.2×10^{-3}		96 hr
1120-71-4	1,3-Propane sultone[a]		8.2×10^{-2}		8.5 hr
94-59-7	Safrole	Zero hydrolysis observed after 26 days at 85°C and pH (3, 7, 11)			
107-49-3	Tetraethyl pyrophosphate[a]		9.3×10^{-2}		7.5 hr
62-55-5	Thioacetamide[a]	$(6.0 \pm 0.06) \times 10^{-2}$	$(8.6 \pm 1.1) \times 10^{-5}$	1.4 ± 0.09	336 d
137-26-8	Thiram		5.0×10^{-3}	4,153 ± 80	5.3 d
8001-35-2	Toxaphene		$(8.0 \pm 2.2) \times 10^{-6}$	3.2 ± 2.2	10 yr
126-68-1	O,O,O-Triethylester phosphorothioic Acid		$(2.0 \pm 0.2) \times 10^{-5}$		3.9 yr
2524-09-6	O,O,S-Triethylester phosporodithioic Acid		$>(2.0 \pm 0.2) \times 10^{-5}$		<3.9 yr
126-72-7	Tris(2,3-Dibromopropyl)-phosphate		$(1.0 \pm 1.1) \times 10^{-5}$	78	4.4 yr

a. Values were extracted from the references in Section 5 for the particular chemical. The neutral hydrolysis rate for thioacetamide was determined at Athens-ERL.

independent of pH, hydrolysis values from the extremes of pH (acid and/or base) were included when calculating the neutral hydrolysis rates reported in Table 6. Confidence limits were calculated from the mean and standard deviation values and are the values reported in Table 6.

Constraints of time, personnel, bath space, and availability of instruments of analysis dictated that rate determinations be confined to shorter periods of time (note the half-lives and temperatures in summary sheets). Ideally, decrease in compound concentration was monitored through three half-lives (<12% remaining); as seen in the summary sheets, some compounds decreased <10% during the period of analysis while others decreased to zero concentration.

An illustrative plot on semi-log paper of % Remaining vs. Time is included with applicable data sheets. Included on the sheet are the pseudo-first-order rate constants, half-life, and r^2.

5.3.1 N-(Aminothioxomethyl)-acetamide

CAS No. 591-08-2

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.28	85	$5.6x10^{-3}$		5.2	.968
3.28	85	$4.5x10^{-3}$		6.4	.979
3.28	85	$4.5x10^{-3}$		6.4	.974
7.16	85	0.51		0.06	.996
7.16	85	0.52		0.06	.999
9.64[a]	25	0.26	1.59	0.11	----
10.54[a]	25	0.90	1.41	0.03	----

Congdon, W. I. and J. T. Edward. 1974. The Alkaline Hydrolysis of N-Acylthioureas. Can. J. Chem. 52, 697-701.

Comments: The hydrolysis rate constant of N-acetylthiourea levels off at higher concentrations of hydroxide ion. A 22,000-fold increase in hydroxide ion concentration caused only a 170-fold increase in the pseudo first-order rate constant. Presumably hydrolysis of N-acetylthiourea involves reaction of the un-ionized molecule (dominant at lower pH) with hydroxide ion.

Water Solubility:

Source: Aldrich

Listed Purity: 99% Identity-Purity comfirmed by spectral analysis.

Analysis Concentration: 2 ppm

Analytical Procedure: N-(Aminothioxomethyl)-acetamide was analyzed by 20-microliter injections onto a Resolvex C_{18} column.

Instrumentation: GC___ HPLC X

Detector: UV at 276 nm

Column: Resolvex C_{18}, 10 micron, 25 cm

Mobile Phase: acetonitrile: water (50:50)

5.3.1 N-(Aminothioxomethyl) -Acetamide

$K_1 = 5.1 \times 10^{-1}\ hr^{-1}$

$T_{1/2} = 1.4\ hr$

$R^2 = 0.999$

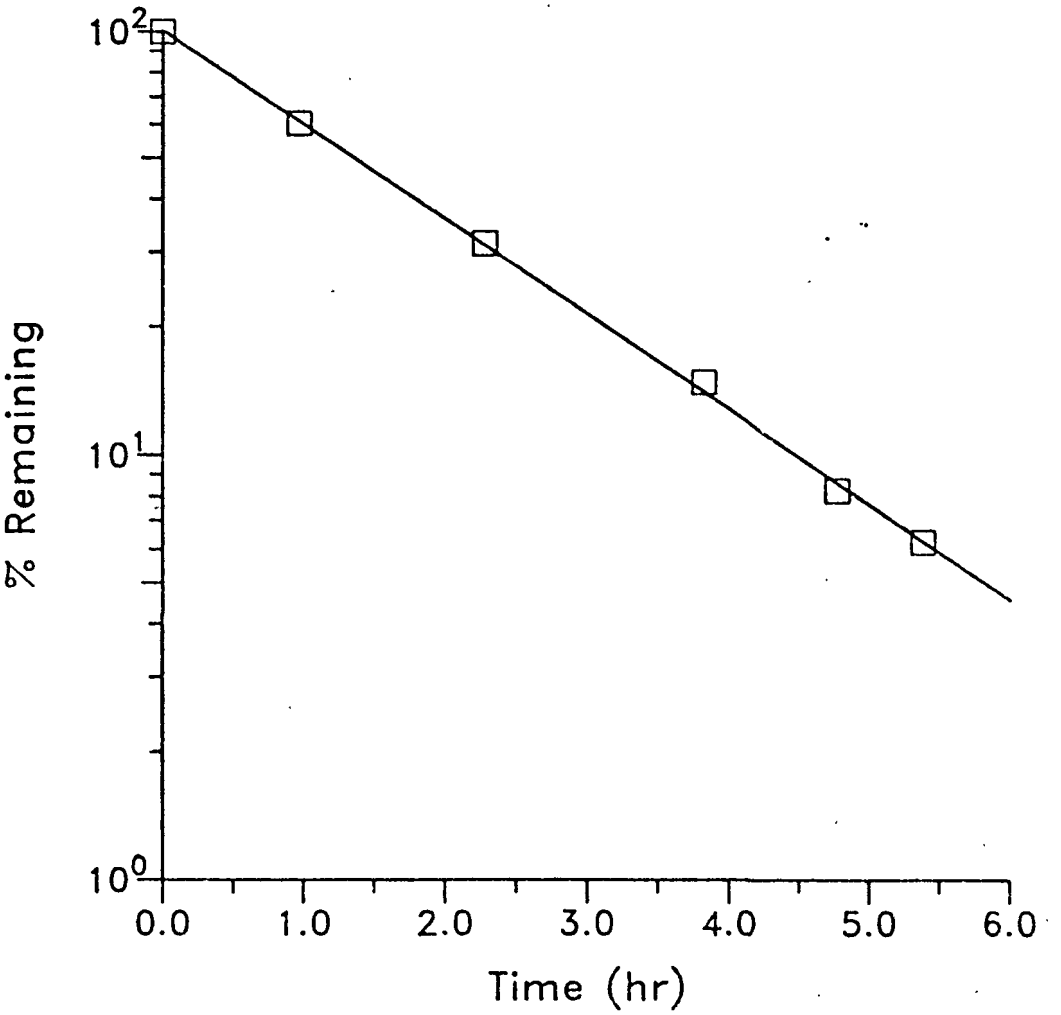

Figure 5.3.1 Hydrolysis of N-(Aminothioxomethyl) -Acetamide at 85°C, pH 7.16

5.3.2 Acetonitrile

CAS No. 75-05-8

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp. °C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}$	r^2
3.26	85.0	No measurable hydrolysis over 31 days.			
6.99	85.0	No measurable hydrolysis over 31 days.			
9.95	85.5	No measurable hydrolysis in 1.5 hours.			
9.95	85.5	No measurable hydrolysis in 1.5 hours.			
10.93	23.0	No measurable hydrolysis in 17.5 hours.			
10.42	66.0	0.0012		24.1 d	----
10.42	66.0	0.0009	0.30*	32.2 d	----
10.13	85.5	0.0082		3.5 d	0.919
10.13	85.5	0.0052	2.80*	5.5 d	0.975

* average of two runs

Comments: Hydrolysis of alkyl nitriles is a known acid or base catalyzed process. A second-order basic hydrolysis rate constant was determined at 66°C and 85°C. The calculated energy of activation (27.7 Kcal/mole) was in good agreement with the value of 28.7 Kcal/mole reported by Gueison (1). The extrapolated second-order alkaline hydrolysis rate constant ($1 \times 10^{-3} M^{-1}hr^{-1}$) is in good agreement with the value measured at 25°C by Peskoff and Meyer ($5.67 \times 10^{-3} M^{-1}hr^{-1}$) (2).

1. Gueison, A. G. and V. A. Linetskii. 1969. Alkaline Hydrolysis of Nitriles. Khim. Prom. (Moscow). 45(4), 264-265.

2. Peskoff N. and J. Meyer. 1913. Zur Kenntnis der Folgereaktionen. III Die Hydrolyse von Saureamiden und Nitrile. Z. Phys. Chem., 82, 129-163.

Water Solubility: Miscible

Source: Aldrich

Listed Purity: 99.9%, confirmed by spectral analysis

Analysis Concentration: 10.8 ppm

Analytical Procedure: Experiments were conducted in 10.0 ml glass sealed ampules to prevent the evaporation of the compound.

Instrumentation: GC X HPLC __

Detector: FID

Column: DBWAX, 1.0 micron film, 30m x 0.53mm ID

Temperature Program: 30°C isothermal

5.3.2 Acetonitrile

$K_1 = 1.25 \times 10^{-1}\ hr^{-1}$
$T_{1/2} = 5.5$ days
$R^2 = 0.974$

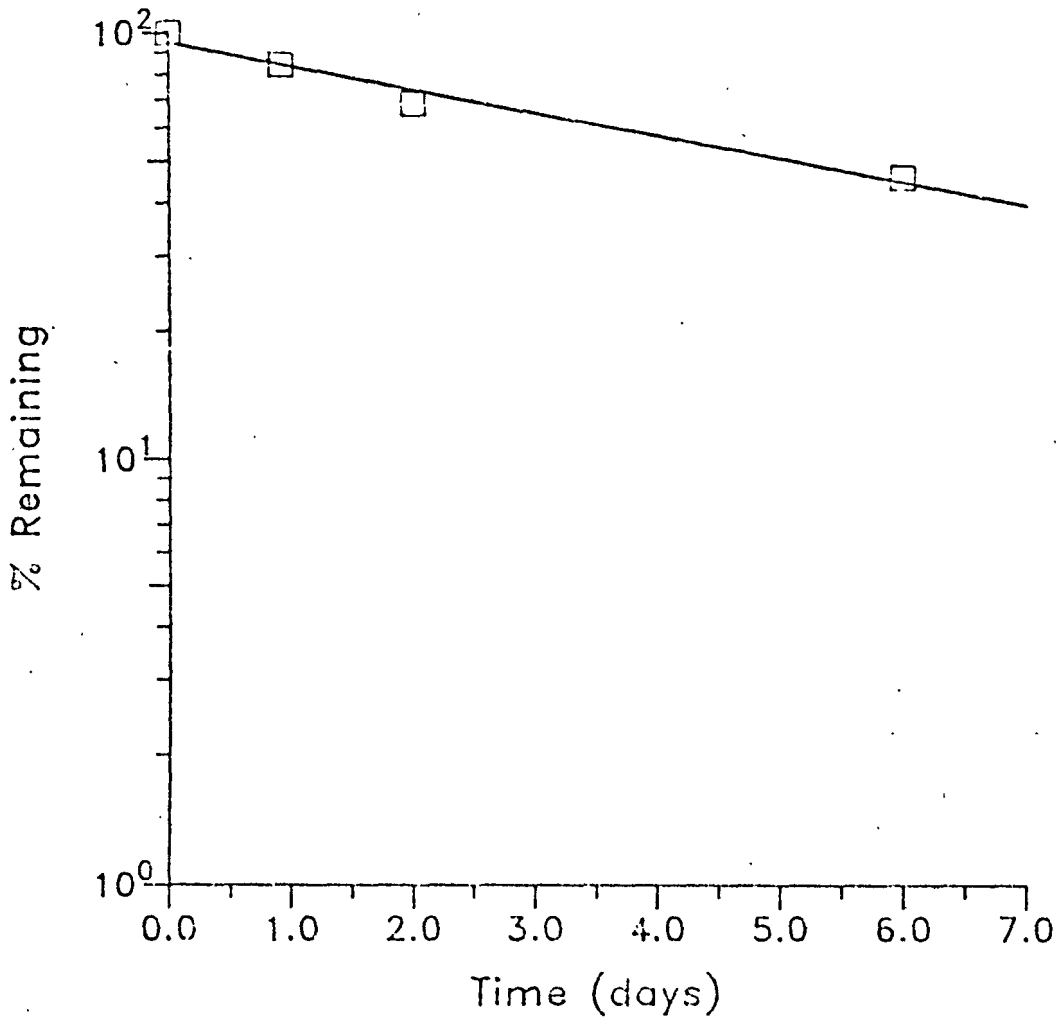

Figure 5.3.2 Hydrolysis of Acetonitrile at 85.5°C pH 10.13

5.3.3 2-Acetylaminofluorene

CAS No. 53-96-3

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
2.97	85.5	0.0019	1.77	365	0.907
2.97	85.5	0.0024	2.24	289	0.932
2.49	85.6	0.0069	2.13	100	0.999
2.49	85.6	0.0073	2.26	95	0.999
7.34	85.5	0.0007		990	0.863
9.80	85.5	0.0024	1.18	289	0.933
9.80	85.5	0.0023	1.13	301	0.982
10.25	85.5	0.0040	0.70	173	0.988
10.25	85.5	0.0042	0.73	165	0.981
10.39	85.6	0.0152	1.93	45	0.999
10.39	85.6	0.0151	1.91	46	0.999
10.39	85.6	0.0516	1.97	44	0.999

Comments: Acetanilides are very stable in aqueous solution. They undergo specific acid and base catalysis with maximum stability in the pH range of 5 to 7.

Water Solubility: 10.13 ± .52 mg/l at 26.3 ± 0.7°C

Source: Aldrich

Identity-purity confirmed by spectral analysis.

Analysis Concentration: 0.3 -- 1.5 mg/L

Analytical Procedure: 0.005M buffered water injected directly onto a 20 microliter injection loop.

Instrumentation: GC ___ HPLC X

Detector: Kratos Spectroflow 757

Column: ODS Ultrasphere, 4.6 mm ID x 15 cm, 5 micron

Mobile Phase: Methanol:water (70:30)

5.3.3 2-Acetylaminofluorene

$K_1 = 6.9 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 4.2$ days
$R^2 = 0.999$

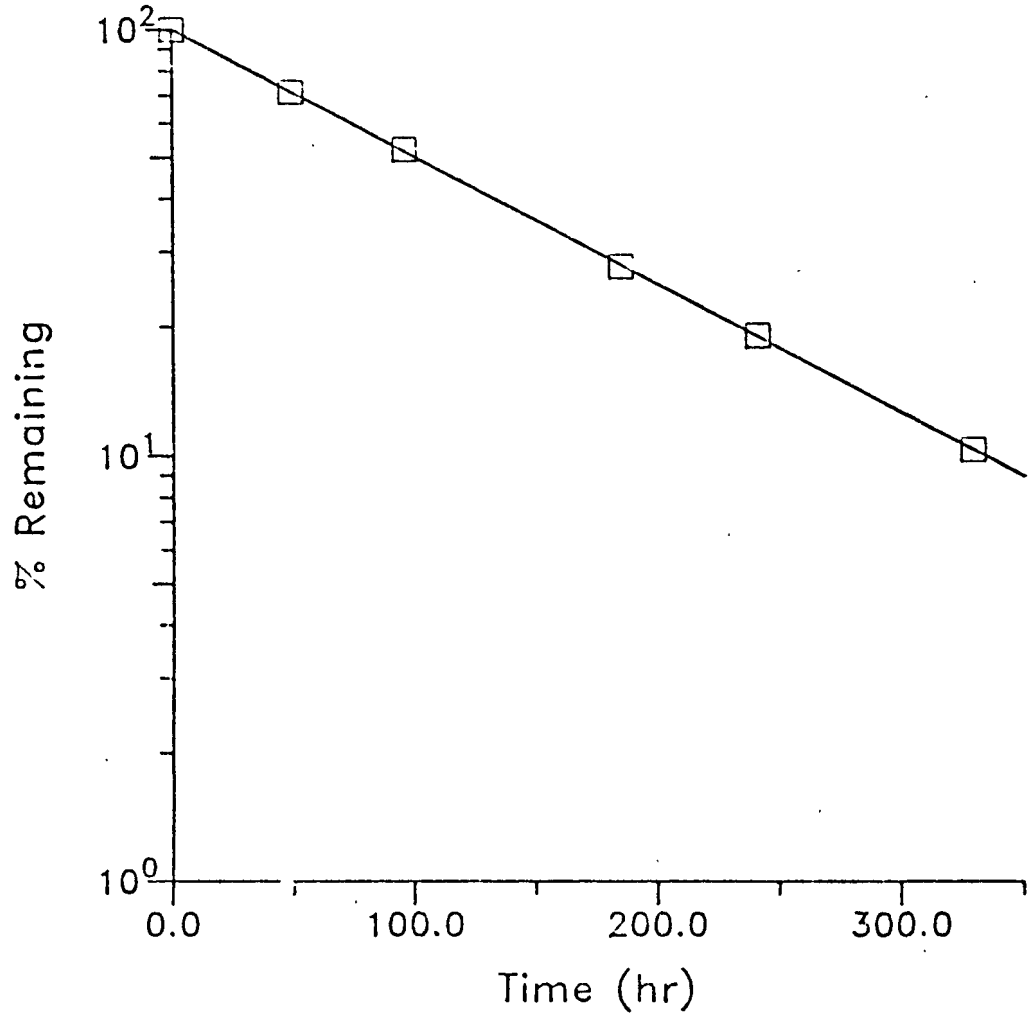

Figure 5.3.3 Hydrolysis of 2-Acetylaminofluoren at 85.6°C, pH 2.49

5.3.4 Auramine

CAS No. 492-80-8

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Auramine is a weak base that forms salts with hydrochloric, sulfuric, and other acids. Auramine decomposes at temperatures above 70°C. Delben et al. (1) reported a second-order acid rate constant of 5.5 M^{-1} hr^{-1}. Holmes and Darling (2) reported the hydrolysis of auramine in neutral solution. The calculated activation energy and hydrolysis rate at 25°C was 23,800 ± 700 cals/mole and 0.00038 hr^{-1} respectively (log A = 14.02 ± 0.51). In alkaline solutions (3) the free imine functional group undergoes a slow reaction with water to yield a carbinol. Equilibrium is reached after a few days at room temperature and is characterized by an equilibrium constant pK = 9.8.

1. Dulben, F., S. Paoletti and V. Crescenzi. 1976. On the Fading of Auramine O in the Presence of Weak Polyacids in Water. Eur. Polym. J. 12, 813-815.

2. Holmes, W. C. and J. F. Darling. 1924. The Hydrolysis of Auramine. J. Am. Chem. Soc. 46, 2343-2345.

3. Goldacre, R. J. and J. W. Phillips. 1949. The Ionization of Triphenylmethane Dyes. J. Chem. Soc., pp. 1724-1732.

5.3.5 Azaserine

CAS No. 115-02-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}$	r^2
3.20	45	1.58	2504	0.43 hr	0.994
3.20	45	1.53	2425	0.43 hr	0.993
3.20	45	1.61	2552	0.43 hr	0.916
3.17	23	0.18	266	3.84 hr	0.988
7.00	65	0.0145		1.99 d	0.952
7.00	65	0.0137		2.11 d	0.928
7.00	65	0.0188		1.53 d	0.821
7.47	84	0.15		4.56 hr	0.997
7.47	84	0.17		4.32 hr	0.997
7.47	84	0.17		4.32 hr	0.999
10.37	66	1.88	608	0.36 hr	0.998
10.37	66	1.73	560	0.41 hr	0.988
10.37	66	2.24	725	0.31 hr	0.999
8.87	85	0.925	3960	0.75 hr	0.922
8.87	85	0.826	3540	0.84 hr	0.998
8.87	85	0.780	3340	0.89 hr	0.993

Comments: Energy of activation and log A for the acid catalyzed hydrolysis is: 19,064 ± 1,683 cals/mole and 16.5 ± 0.14 respectively. The hydroxide catalyzed hydrolysis yielded an activation energy of 22,150 cals/mole and log A = 17.08 ± 0.94.

Water Solubility: > 1.0 g/L

Source: Sigma

Listed Purity: None stated

Analysis Concentration: 7 mg/L

Analytical Procedure: Azaserine was analyzed by direct injection of 20 ml of solution into Zorbax NH_2 column for each sample.

Instrumentation: GC ___ HPLC X

Detector: UV at 252 nm

Column: Zorbax NH_2 (25 cm) or micro-Bundapak C_{18} (30 cm)

Mobile Phase: Methanol: 0.05 M NaH_2PO_4 (50:50)

5.3.5 Azaserine

$K_1 = 2.2\ hr^{-1}$
$T_{1/2} = 0.3\ hr$
$R^2 = 0.999$

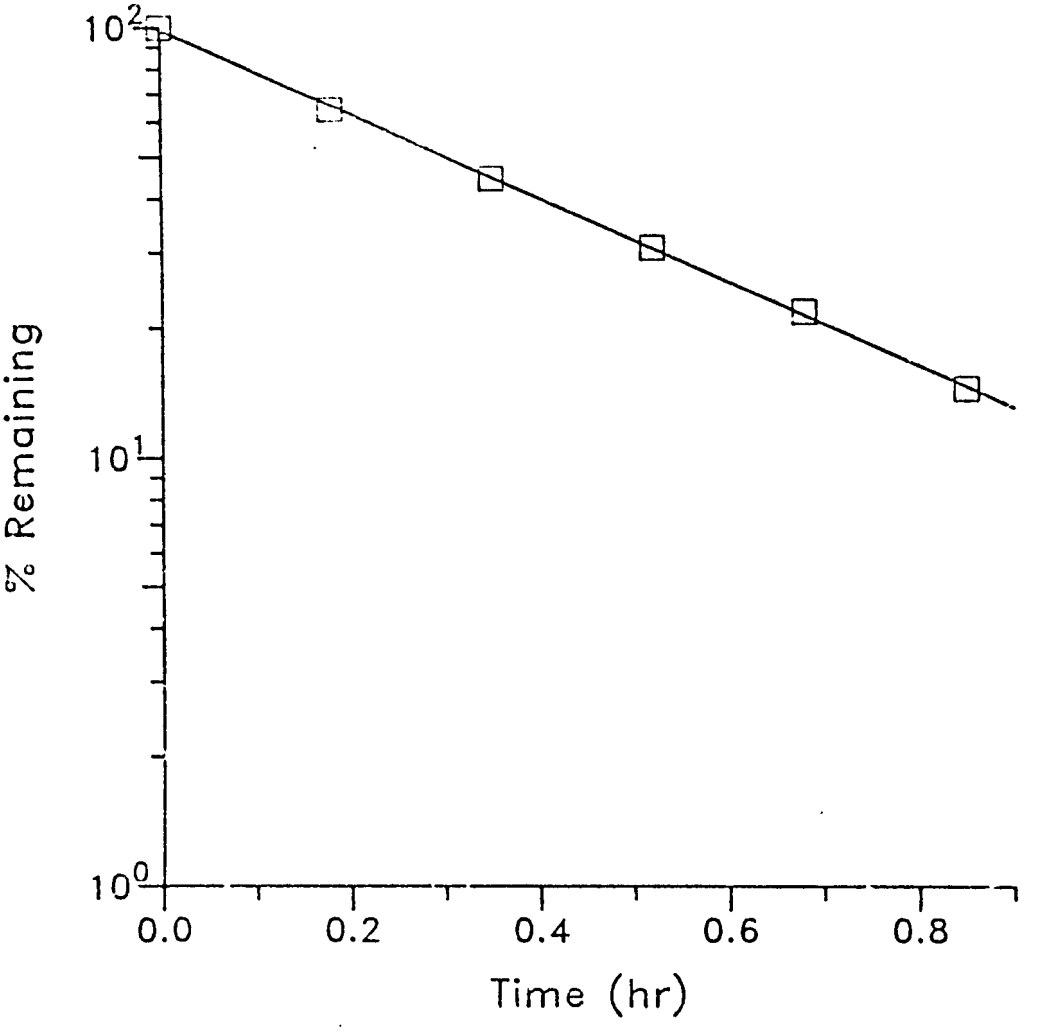

Figure 5.3.5 Hydrolysis of Azaserine at 66°C, pH 10.37

5.3.6 Chlorambucil

CAS No. 305-03-3

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Chlorambucil is one of a series of nitrogen mustards tested as anticancer drugs (5.3.8, 5.3.13, and 5.3.34). Hopwood and Stock (1) reported a neutral hydrolysis rate constant of 0.38 hr^{-1} at 25°C (half-life 1.8 hr).

1. Hopwood, W. J. and J. A. Stock. 1971/1972. The Effect of Macromolecules upon the Rates of Hydrolysis of Aromatic Nitrogen Mustard Derivatives. Chem. Biol. Interactions. 4, 31-39.

5.3.7 Chlordane

CAS No. 57-74-9

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data: cis-Chlordane[2]

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
10.18	84.0	0.36	78.8	0.08	0.986
10.18	84.0	0.34	74.4	0.08	0.989
10.18	84.0	0.32	70.0	0.08	0.977
10.85	65.0	0.04	4.7	0.70	0.995

1. 57-74-9 is CAS No. for technical chlordane

2. Zero degradation was observed for trans-chlordane during five days at pHs of 3, 7, and 11 and at 85°C. The only degradation observed with cis-chlordane is reported above.

Comments: The two major components of technical chlordane are the cis and trans isomers. The data above are consistent with the structures of the isomers. cis-Chlordane (CAS No. 5103-74-2) is more susceptible to hydroxide catalyzed dehydrohalogenation because the 1-exo, 2-exo orientation of the chlorine atoms facilitates the E_2 elimination of HCl. The trans isomer (CAS No. 5103-71-9) has 1-exo, 2-endo orientation of the chlorine atoms and thus does not undergo E_2 elimination. Calculated activation energy for alkaline hydrolysis of cis-chlordane is E_a = 34,966 ± 1,800 cals/mole, log A = 23.3 ± 0.10.

Water Solubility: 56 ppb

Source: RTP

Listed Purity:

Analysis Concentration: 5 ppb in H_2O

Analytical Procedure: Extract 10 ml buffer with 1 ml 50 ppb Endosulfan II in isooctane. Add 2 ml isooctane and shoot.

Extraction Solvent: isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: OV-1, 2.65 M, 0.53mm ID, 5m long

Temperature Program: 190°C isothermal

Mobile Phase: N/A

Internal Standard: Endosulfan - II, 17 ppb

5.3.7 α–Chlordane

$K_1 = 4.1 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 0.7$ days
$R^2 = 0.995$

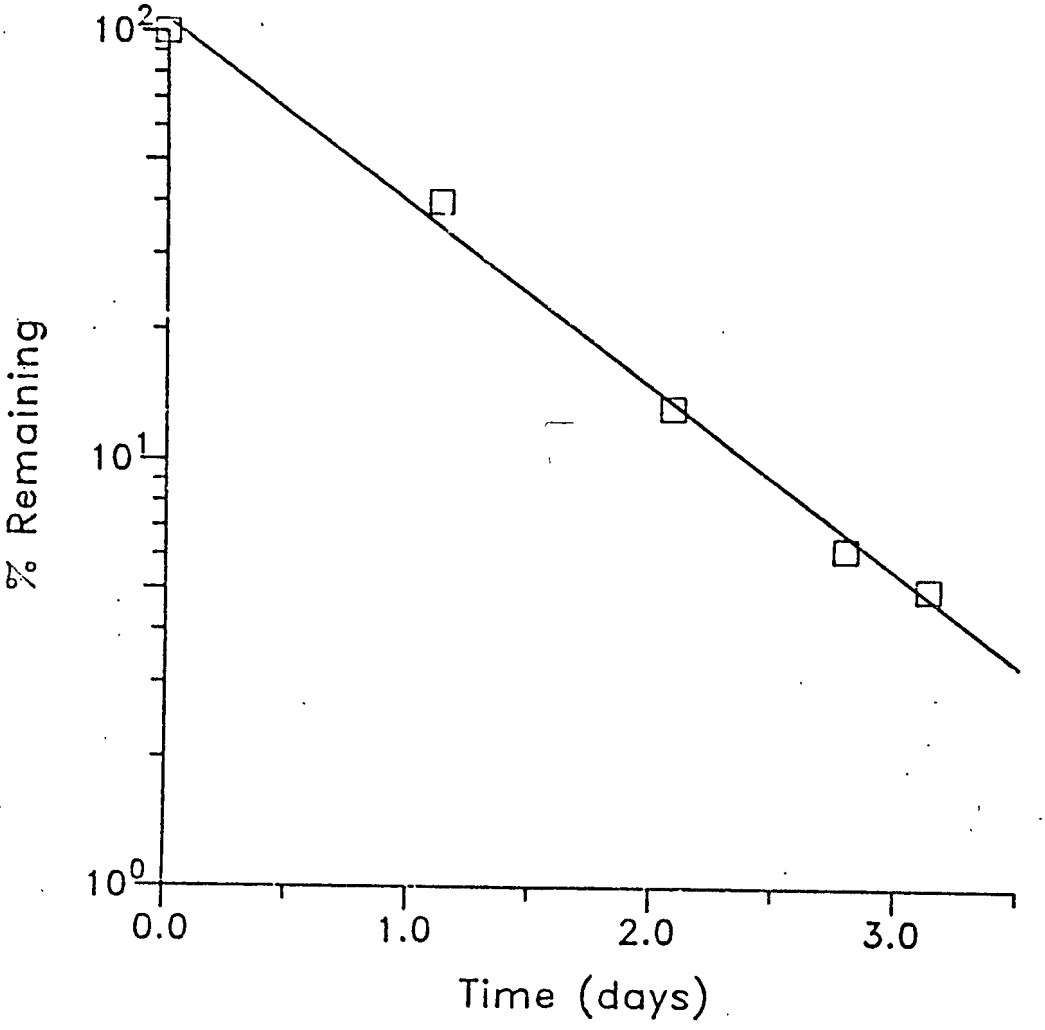

Figure 5.3.7 Hydrolysis of α–Chlordane at 65°C, pH 10.85

5.3.8 Chlornaphazine

CAS No. 494-03-1

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Chlornaphazine, a nitrogen mustard, undergoes netural hydrolysis with a half-life of 216 hours (1).

1. Ghielmetti, G. 1950. Caratteristiche Di Una Azotoiprite Aromatica La Bis(2-chloroetil)-β-Naftilamina. Farmaco Ed. Sci. 5, 275-280.

5.3.9 Beta-Chlornaphthalene

CAS No. 91-58-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$X10^3 k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
3.04	85.5	4.23		163.0	0.977
3.14	85.5	1.51		459.0	0.959
3.19	85.5	1.10		630.0	0.880
2.93	85.8	2.72		255.0	0.989
2.93	85.8	2.46		281.0	0.964
7.10	85.5	4.44		156.0	0.978
7.14	85.8	3.28		211.0	0.873
7.30	85.5	1.25		554.0	0.971
7.30	85.5	2.03		341.0	0.928
7.06	85.5	1.23		563.0	0.729
7.06	85.5	1.25		554.0	0.660
9.65	86.0	6.60		105.0	0.661
9.58	85.5	2.84		244.0	0.985
9.75	85.5	3.46		200.0	0.974
9.75	85.5	1.81		382.0	0.978
9.51	85.6	3.50		198.0	0.822

Comments: Data for all pHs were combined and used to calculate the neutral hydrolysis rate constant.

Source: RTP lot No. 0130

Listed Purity: 99%

Analysis Concentration: 1.6 ppm

Analytical Procedure: Extract 10 ml of aqueous sample with 3.0 ml isooctane. Dilute extract 1:1 with internal standard solution (2,4-D methyl ester 200 ppb).

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: DB-1 30m, .32mm ID

Temperature Program: 170° Isothermal

Internal Standard: 2,4-D Methyl ester at 100 ppb

5.3.9 B-Chloronapthalene

K_1 = 1.2×10^{-3} hr^{-1}
$T_{1/2}$ = 23 days
R^2 = 0.9706

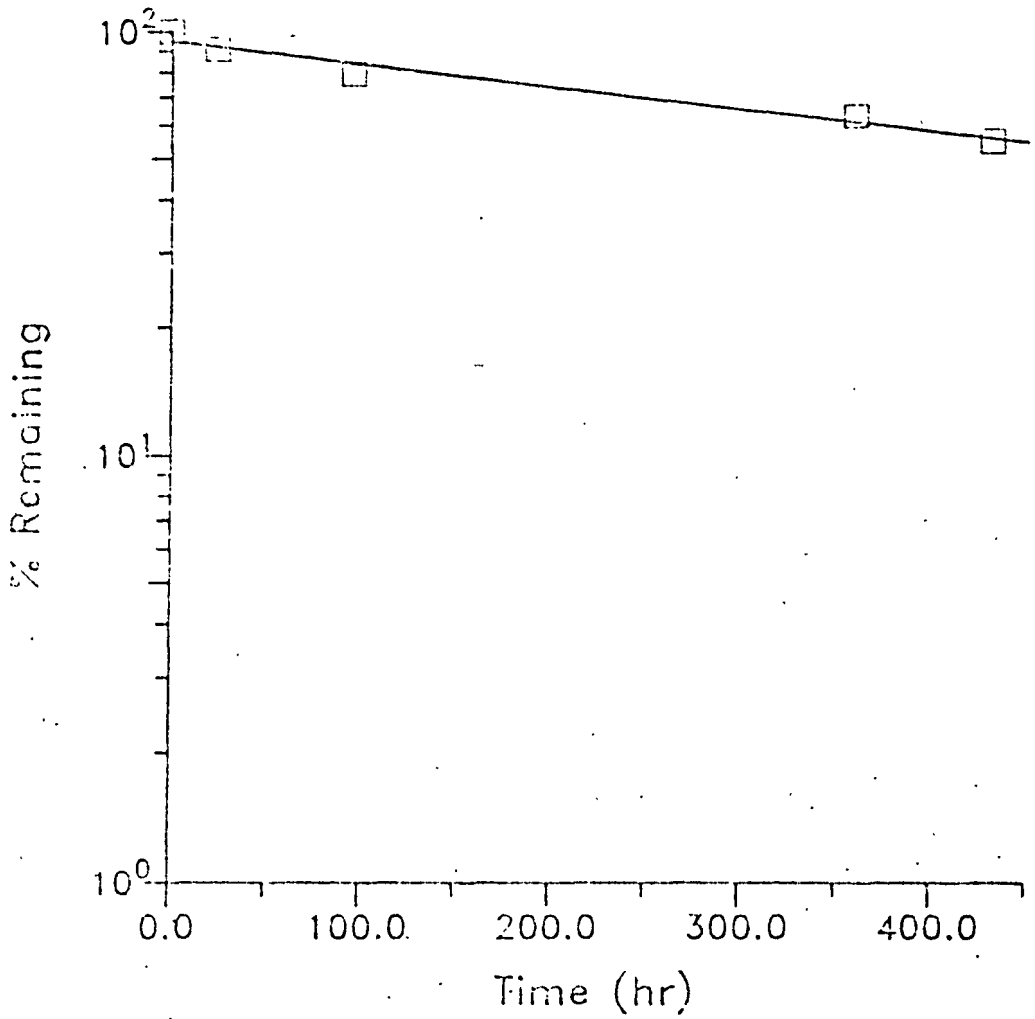

Figure 5.3.9 Hydrolysis of B-Chloronapthalene at 35.5°C, pH 7.30

5.3.10 2-Chloro-1,3-butadiene

CAS No. 126-99-8

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Chloroprene (2-Chloro-1,3-butadiene) polymerizes spontaneously at room temperature and forms cylic dimers on prolonged standing in the presence of polymerization inhibitors (1). Chloroprene is stable to hydrolysis. On refluxing with concentrated alcoholic sodium hydroxide, alcoholic silver nitrate, or pyridine, only traces of chlorine are split off (2).

1. Bauchuritz, P.S. 1964. Chloroprene. In: Kirk, R. E. and Othmer, D. F., eds., Encyclopedia of Chemical Technology, 2nd ed., Vol. 5, New York, John Wiley and Sons, pp. 215-231.

2. Carothers, W. H., I. Williams, A. M. Collins and J. E. Kirby. 1931. Acetylene Polymers and their Derivatives II. A New Synthetic Rubber: Chloroprene and its Polymers. J. Am. Chem. Soc. 53, 4203-4225.

5.3.11 1-(O-chlorophenyl)thiourea

CAS No. 5344-82-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$X10^3 k_1 (hr^{-1})$	$k_2 (M^{-1}hr^{-1})$	$t_{1/2}$(hr)	r^2
3.24	85	0.010		2.9	0.914
3.24	85	0.011		2.7	0.994
3.24	85	0.011		2.7	0.969
7.16	85	0.015		1.9	0.996
7.16	85	0.019		1.5	0.967
7.16	85	0.019		1.6	0.912
7.09	65	0.0007		40.1	0.956
7.09	65	0.0013		22.7	0.860
9.57	85	0.044	41.1	0.7	0.986
9.57	85	0.048	44.8	0.6	0.977
9.57	85	0.041	38.3	0.7	0.988

Comments: Calculated energy of activation and log A for hydrolysis at pH 7 was 34,482 ± 7.295 cals/mole and 19.29 ± 3.05, respectively. Extrapolation to 25°C was based on E_a = 34,482 cals/mole.

Source: Aldrich

Listed Purity: 98% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 2 ppm

Analytical Procedure: Direct injection onto HPLC column, high pH samples were neutralized before analysis.

Instrumentation: GC ___ HPLC X

Detector: UV at 264 nm

Column: Nova Pak C_{18}

Mobile Phase: Acetonitrile:Water (50:50)

5.3.11 1-(o-Chlorophenyl) thiourea

K_1 = 4.4 x 10^{-2} hr^{-1}

$T_{1/2}$ = 0.7 days

R^2 = 0.986

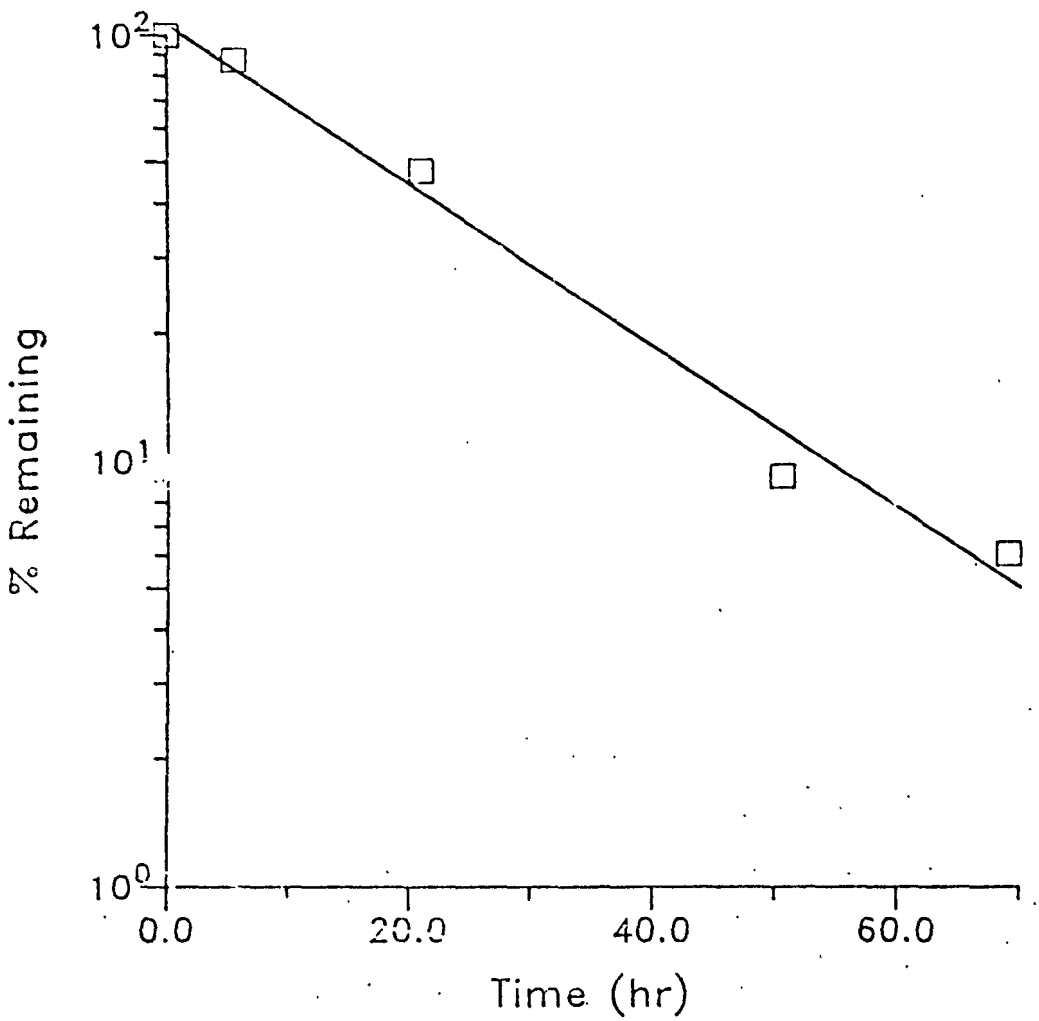

Figure 5.3.11 Hydrolysis of 1-(o-Chlorophenyl) thiourea at 85°C, pH 9.57

5.3.12 3-Chloropropanenitrile

CAS No. 542-76-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}$	r^2
3.22	85.5	0.0029		9.8 d	0.995
3.22	85.5	0.0035		8.2 d	0.987
3.22	85.5	0.0036		8.1 d	0.975
3.15	85.1	0.0026		11.1 d	0.968
3.15	85.1	0.0036		8.0 d	0.974
6.92	45.4	0.0344		20.1 hr	0.995
6.92	45.4	0.0278		24.9 hr	0.999
6.92	45.4	0.0274		25.3 hr	0.994
6.92	45.4	0.0249		27.8 hr	0.999
7.19	85.5	None left at first time point.			
7.01	65.6	0.422		1.7 hr	0.982
7.01	65.6	0.401		1.7 hr	0.993
7.04	65.0	0.443		1.6 hr	0.967
7.04	65.0	0.463		1.5 hr	0.993
9.82	85.5	None left at 0 time point.			
10.49	45.4	None left at 0 time point.			
10.49	45.4	None left at 0 time point.			
8.56	25.5	0.0491	13004	14.1 hr	0.941
8.56	25.5	0.0407	10779	17.0 hr	0.989
9.11	25.5	0.1774	13241	3.9 hr	0.984
9.11	25.5	0.1509	11263	4.6 hr	0.978

Water Solubility: 45000 mg/L at 25°C

Source: Aldrich

Listed Purity: 98% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 2.0 ppm -- 15.4 ppm

Analytical Procedure: 3-Chloropropanenitrile was analyzed by direct aqueous injections on GC for each sample analysis. The buffer concentration was .02 M.

Instrumentation: GC X HPLC ___

Detector: FID

Column: DBWAX, 1.0 micron, 30m x 0.53mm ID

Temperature Program: 90°C to 160°C at 40°C/min hold for 6 min at 160°C.

Internal Standard: Malononitrile at 10.4 ppm

5.3.12 3-Chloropropanenitrile

$K_1 = 6.7 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 1.7\ hr$
$R^2 = 0.993$

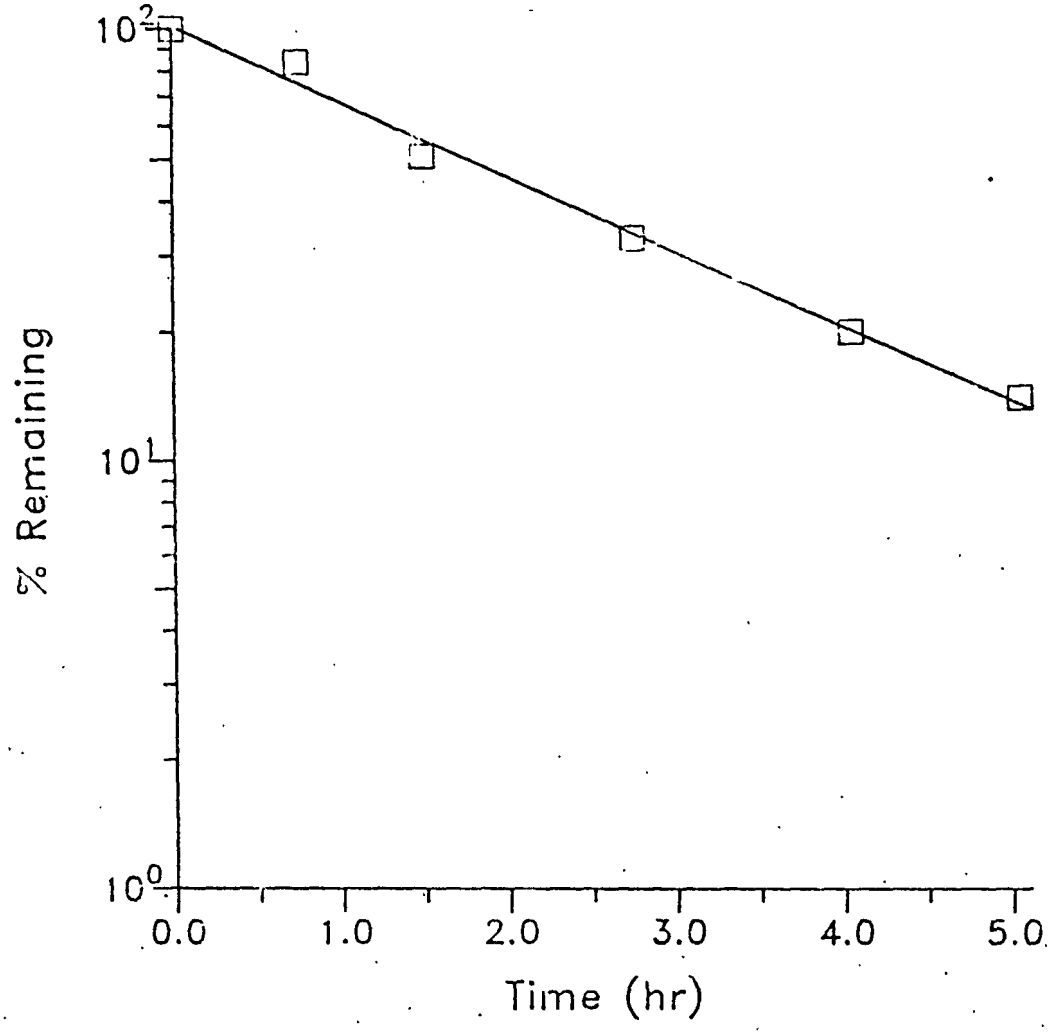

Figure 5.3.12 Hydrolysis of 3-Chloropropanenitrile at 22.8°C, pH 7.01

5.3.13 Cyclophosphamide

CAS No. 50-18-0

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

The hydrolysis of cyclophosphamide is independent of pH in the pH 3-10 region. Kensler (1) reported a neutral hydrolysis rate constant of 7.14×10^{-4} hr^{-1} and activation energy of 25,000 cals/mole. The half-life at pH 7 and 25°C is 40 days.

1. Kensler, T. T., R. J. Behme and D. Brooke. 1979. High-Performance Liquid Chromatographic Analysis of Cyclophosphamide. J. Pharm. Sci. 68, 172-174.

5.3.14 DDD (p,p' isomer)

CAS No. 72-54-8

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$X10^3 k_1 (hr^{-1})$	$k_2 (M^{-1}hr^{-1})$	$t_{1/2}$(d)	r^2
3.21	85	1.0		28.8	0.800
3.21	85	0.9		31.9	0.842
3.21	85	0.5		60.0	0.886
7.22	85	4.9		5.9	0.997
7.22	85	5.4		5.3	0.999
7.22	85	4.6		6.3	0.994
9.67	85	731	495	0.04	0.985
9.67	85	867	579	0.03	0.999
9.67	85	622	420	0.05	0.974
10.26	65	291	127	0.10	0.975
10.26	65	305	133	0.09	0.994

Comments: The calculated energy of activation for basic hydrolysis is E_a = 16,148 ± 2,051 cals/mole, log A = 12.5 ± 0.7.

Water Solubility:

Source: RTP

Listed Purity: 99%

Analysis Concentration: 4.6 µg/L Confirmed by spectral analysis.

Analytical Procedure: Extract 10 ml buffer with 2 ml (7 µg/L) Endosulfan I in isooctane. Final analysis concentration was 24 µg/L DDD and 7.2 µg/L Endosulfan I.

Extraction Solvent: Isooctane

Instrumentation: GC X

Detector: ECD

Column: OV-1, 2.65 micron film, 5m x 0.53mm ID

Temperature Program: 200°C isothermal

Internal Standard: Endosulfan I

5.3.14 DDD

$K_1 = 4.9 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 5.9$ days
$R^2 = 0.997$

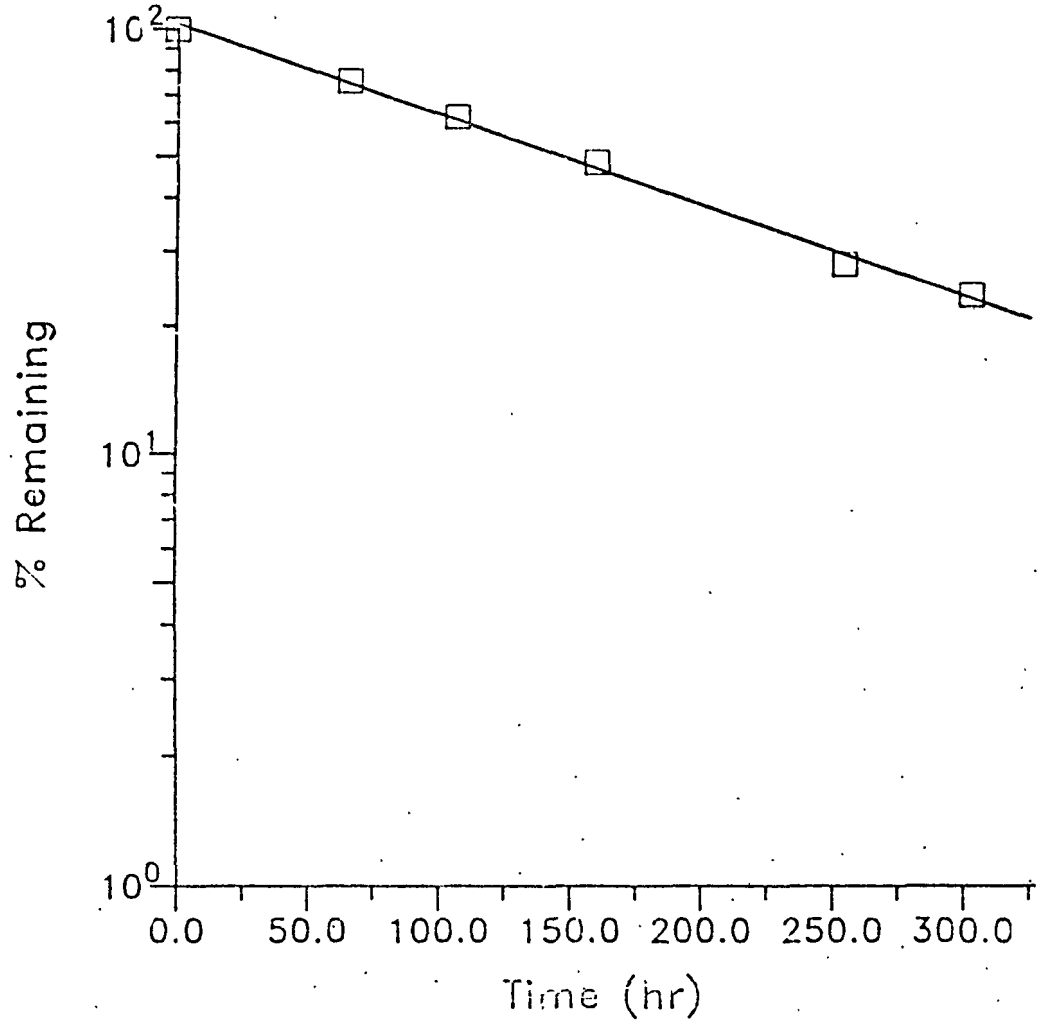

Figure 5.3.14 Hydrolysis of DDD at 85°C, pH 7.22

5.3.15 Daunomycin

CAS No. 20830-81-3

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.21	85	0.039		0.73	0.953
3.21	85	0.038		0.76	0.955
3.21	85	0.040		0.72	0.944
7.09	85	0.027		1.07	0.994
7.09	85	0.027		1.05	0.990
7.09	85	0.029		1.01	0.997
9.18	85	1.63	3420	0.02	0.936
9.18	85	1.42	2990	0.02	0.988
9.18	85	1.60	3350	0.02	0.979
9.70	65	0.45	710	0.06	0.927
9.70	65	0.37	600	0.08	0.963
9.70	65	0.29	460	0.10	0.938

Comments: The calculated energy of activation for base catalyzed hydrolysis is: E_a = 20,455 ± 3,671 cals/mole and the log A = 15.0 ± 1.40.

Water Solubility: Daunomycin hydrochloride is readily soluble in water.

Source: Fluka

Listed Purity: Not stated

Analysis Concentration: 3.6 mg/L

Analytical Procedure: Daunomycin was analyzed by direct injection of 20 microliters of each sample.

Instrumentation: GC ___ HPLC X

Detector: UV at 532 nm

Column: Nova-Pak C_{18}, 15 cm

Mobile Phase: acetonitrile:water (50:50) with .005 M Pic B 8

5.3.15 Daunomycin

$K_1 = 1.4\ hr^{-1}$
$T_{1/2} = 0.5\ hr$
$R^2 = 0.988$

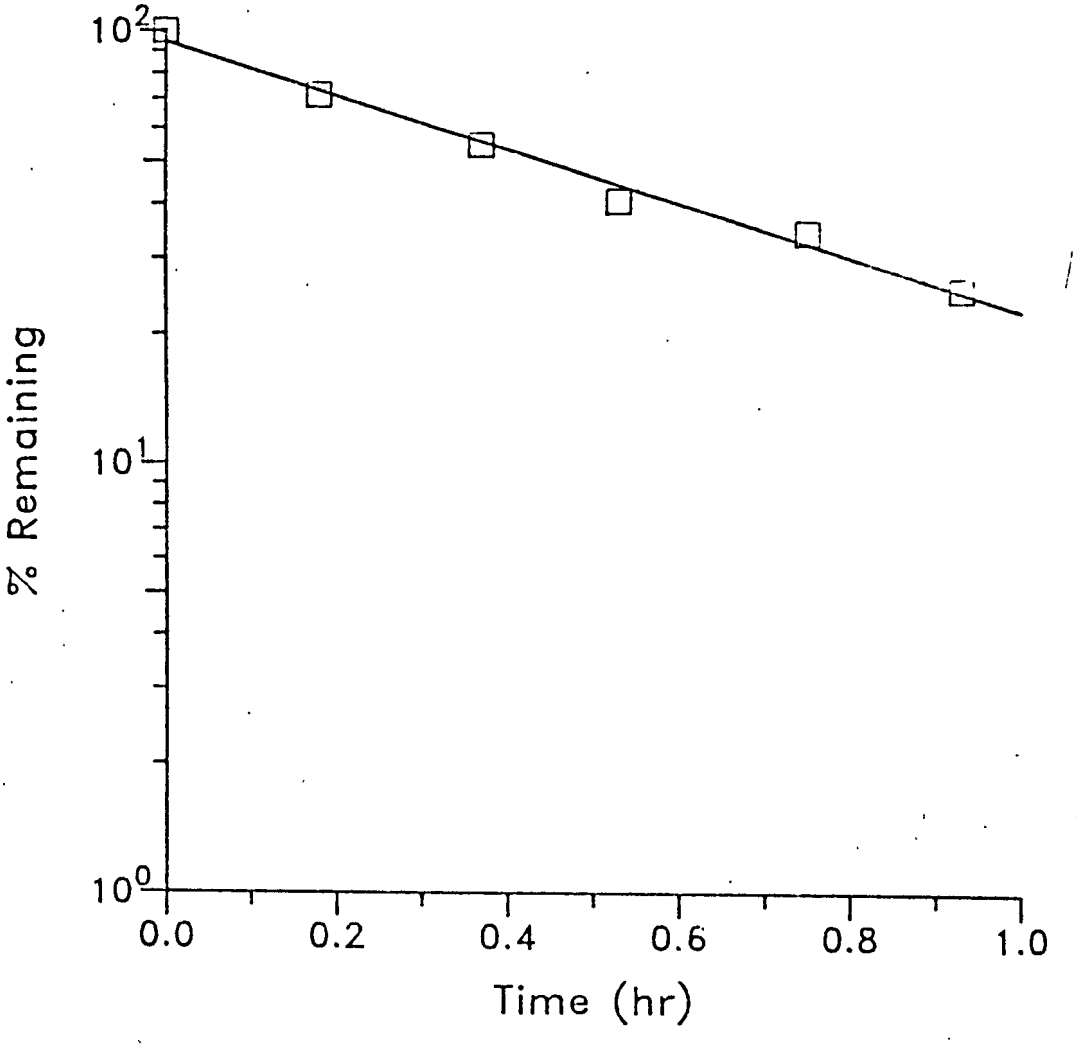

Figure 5.3.15 Hydrolysis of Daunomycin at 85°C
pH 9.18

5.3.16A Cis-Diallate

CAS No. 2303-16-4*

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.07	65.0	0.004		7.20	0.927
3.09	65.1	0.005		5.80	0.933
3.12	85.0	0.140		0.21	0.900
3.02	85.0	0.118		0.24	0.998
7.08	65.3	0.005		5.80	0.996
6.98	65.1	0.015		1.90	0.960
7.04	85.0	0.101		0.28	0.961
7.09	85.0	0.052		0.56	0.810
9.87	65.0	0.012		2.30	0.932
9.61	85.0	0.039		0.73	0.888
9.61	85.0	0.033		0.88	0.919
9.65	85.0	0.033		0.88	0.977

5.3.16B Trans-Diallate

CAS No. 2303-16-4*

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.07	65.0	0.004		7.90	0.934
3.09	65.1	0.006		4.80	0.927
3.02	84.3	0.115		0.25	0.997
3.12	85.0	0.139		0.21	0.893
7.08	65.3	0.005		5.80	0.988
6.98	65.1	0.015		1.90	0.974
7.04	85.0	0.101		0.28	0.960
7.09	85.0	0.055		0.53	0.741
9.61	85.0	0.299	233	0.09	0.888
9.61	85.0	0.302	235	0.09	0.919
9.65	85.5	0.456	318	0.06	0.918

*Mixture of cis and trans isomers

Comments: Smith and Fitzpatrick (1) reported the complete breakdown of diallate at 75°C in 12N sulfuric acid and 1N sodium hydroxide. Diallate contains approximately equal amounts of the cis and trans isomers. Under the much milder conditions employed in our hydrolysis studies, the hydrolysis mechanism and rate under acidic and neutral conditions were essentially the same. Hydrolysis of the trans isomer was catalyzed by hydroxide ion while the cis isomer hydrolysis was retarded by a factor of three.

1. Smith, A. E. and Anne Fitzpatrick. 1970. The Loss of Five Thiolcarbamate Herbicides in Nonsterile Soils. J. Agr. Food Chem. 18, 720-722.

Water Solubility: 14 mg/L^{-1} at 25°C

Source: EPA

Listed Purity: 100% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 500 µg/L

Analytical Procedure: Extract buffered diallate solution with 1 ml internal standard solution (1.9 mg/L Zinophos in acetonitrile). Dilute 1:5 with isooctane.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: NPD

Column: 15m, 0.53mm ID, DB-5, 1 micron film

Temperature Program: 140° - 180°C at 5°/min, hold 10 min at 180°C.

Mobile Phase: N/A

Internal Standard: 1.9 ppm Zinophos in acetonitrile.

5.3.16A cis-Diallate

$K_1 = 5.6 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 5.2$ days
$R^2 = 0.934$

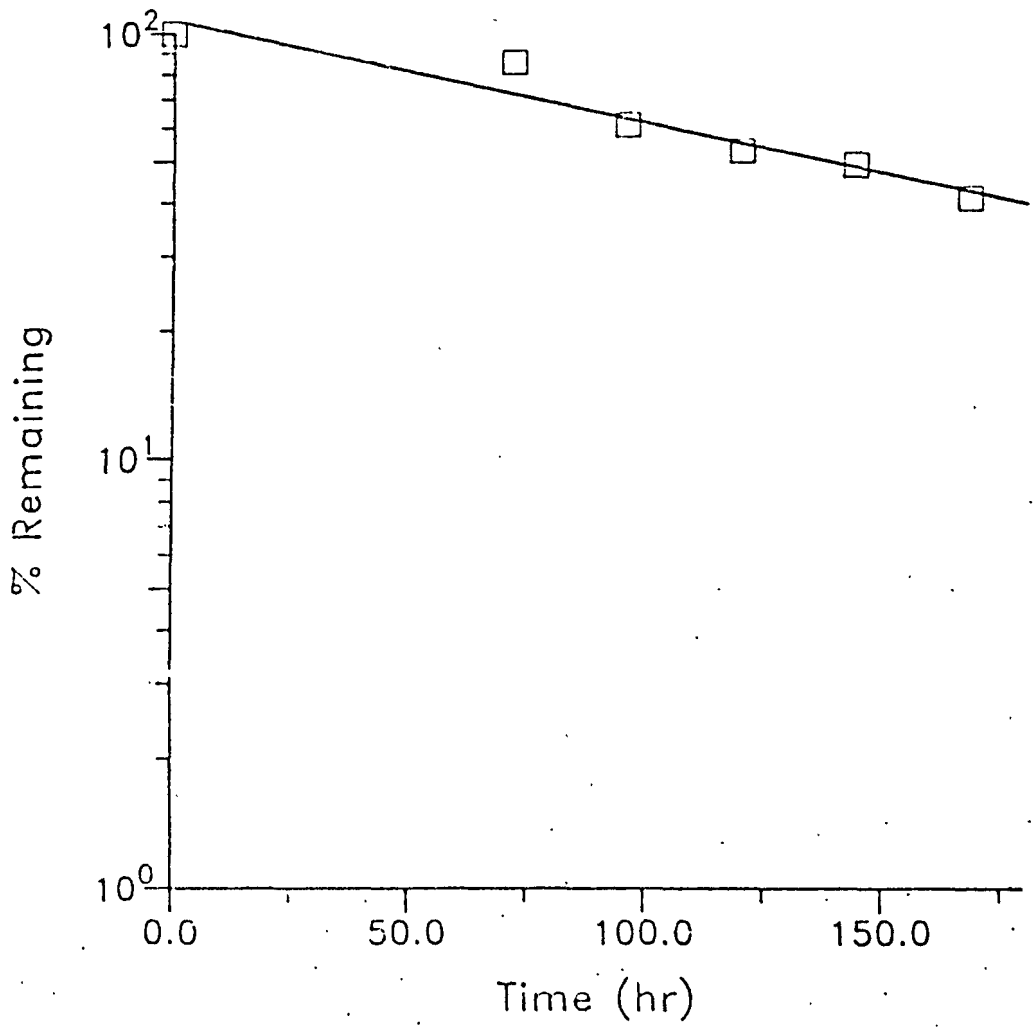

Figure 5.3.16A Hydrolysis of cis-Diallate at 65°C pH 3.09

5.3.16B trans-Diallate

$K_1 = 5.6 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 5.1$ days
$R^2 = 0.927$

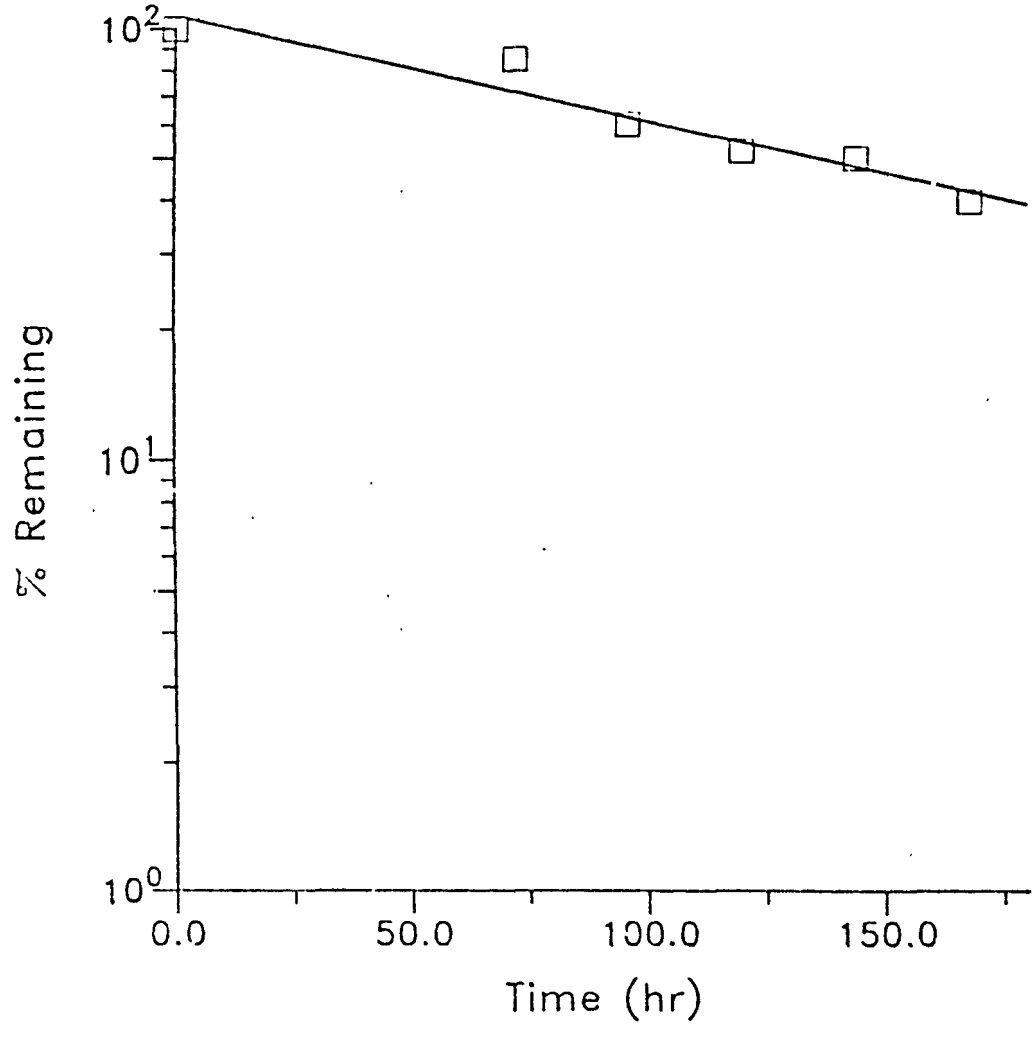

Figure 5.3.16B Hydrolysis of trans-Diallate at 65°C, pH 3.09

5.3.17 Dichloroethyl ether

CAS No. 111-44-4

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Van Duuren et al. (1) measured a netural hydrolysis rate of 0.032 hr^{-1} and half-life of 21 hours at 25°C.

1. Van Duuren, B. L., C. Katz, B. M. Goldschmidt, K. Frenkel and A. Sirak. 1972. Carcinogenicity of Halo-ethers. II Structure-Activity Relationships of Analogs of Bis(chloromethyl)ether. J. Nat. Cancer Inst. 48, 1431-1439.

5.3.18 1,2-Dichloropropane

CAS No. 78-87-5

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$X10^3 k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.19	85	1.39		21	0.913
3.21	85	1.72		17	0.944
3.21	85	1.46		20	0.970
7.20	85	1.47		20	0.973
7.15	85	1.69		17	0.953
7.15	85	1.22		24	0.986
9.60	85	2.99	2.60	10	0.977
9.60	85	3.16	2.75	9	0.971
9.60	85	2.73	2.37	11	0.936
9.96	66	0.26	0.24	111	0.785
9.96	66	0.27	0.24	107	0.831

Comments: The calculated energy of activation for basic hydrolysis is 30,700 cals/mole. The extrapolated basic K_2 at 25°C is 4.3×10^{-4} M^{-1} hr^{-1}.

Water Solubility:

Source: Aldrich

Listed Purity: 99% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 0.31 ppm

Analytical Procedure: Extract 10 ml buffer with 1 ml 102 µg/L 1,3-dibromopropane in isooctane. Dilute 1:1 with isooctane and analyze. Final concentration was 1.5 ppm 1,2-dichloropropane and 51 µg/L 1,3-dibromopropane.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: DB-5, 5 micron film, 15m x 0.53mm

Temperature Program: 75°C for 2 min to 250°C for 1 min at 12°C/min

Internal Standard: 1,3-dibromopropane

5.3.18 1,2-Dichloropropane

$K_1 = 1.2 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 24$ days
$R^2 = 0.986$

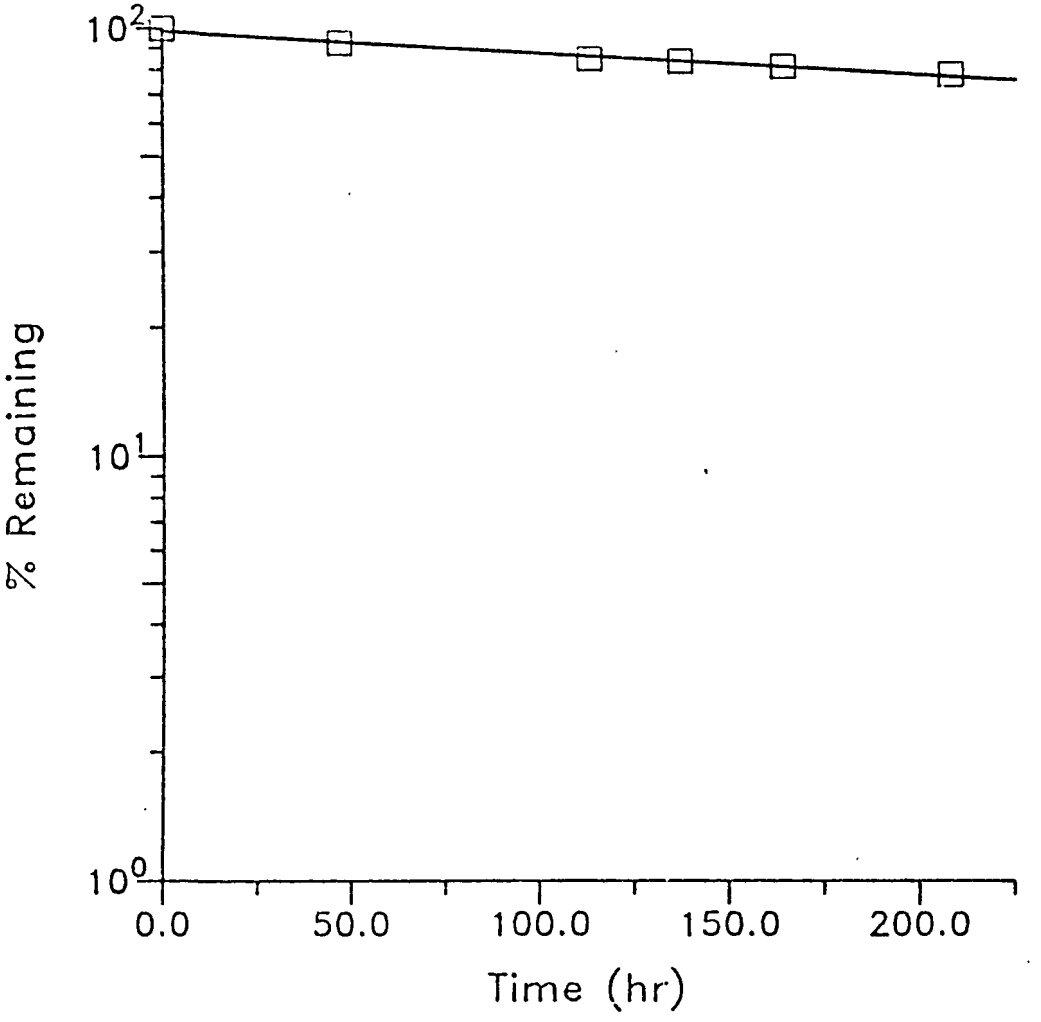

Figure 5.3.18 Hydrolysis of 1,2-Dichloropropane at 85°C, pH 7.15

5.3.19 O,O-Diethyl-O-pyrazinyl phosphoro thioate

CAS No. 297-97-2

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.12	85	0.18		0.16	0.978
3.12	85	0.16		0.18	0.978
3.12	85	0.16		0.18	0.987
7.22	85	0.19		0.16	0.992
7.15	85	0.16		0.16	0.997
7.15	85	0.17		0.17	0.994
7.15	85	0.17		0.17	0.998
10.00	65	0.42	335	0.07	0.985
10.00	65	0.41	323	0.07	0.998
10.00	65	0.38	304	0.07	0.972
10.00	65	0.37	261	0.08	0.974

Water Solubility:

Source: RTP

Listed Purity: 98.7% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 95 µg/L

Analytical Procedure: Extract 10 ml buffer with 3 ml of 0.52 ppm Disulforon in iso-octane

Extraction Solvent: Isooctane

Instrumentation: GC X

Detector: NPD

Column: 30m OV-1, 1.0m film, 0.32mm ID

Temperature Program: 160°C for 3 min then 10°C per min to 220°C hold at 220°C for 10 min.

Internal Standard: Disulfoton

5.3.19 O,O-Diethyl-O-pyrazinyl phosphorothioate

$K_1 = 4.1 \times 10^{-1}\ hr^{-1}$

$T_{1/2} = 1.7$ hr

$R^2 = 0.998$

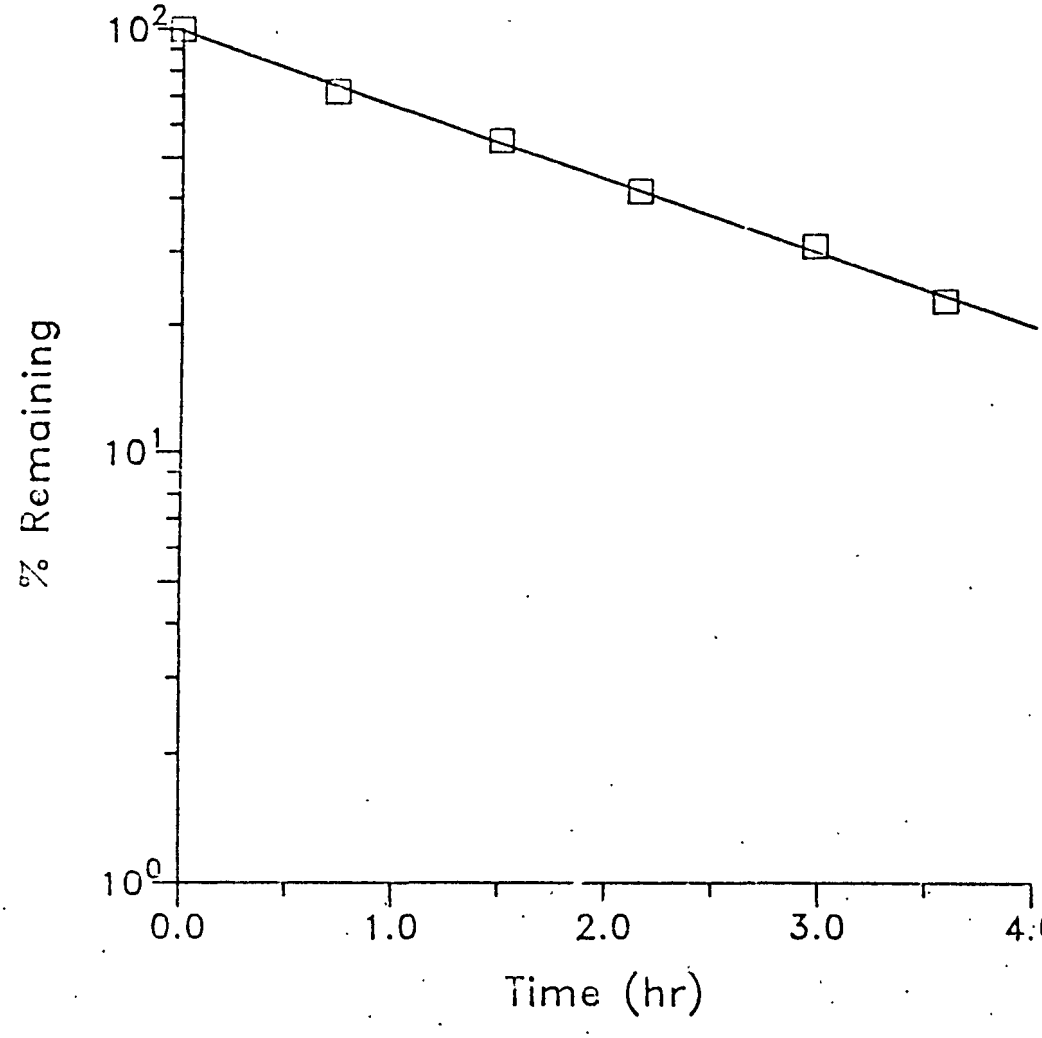

Figure 5.3.19 Hydrolysis of O,O-Diethyl-O-pyraziny phosphorothioate at 65°C, pH 10.00

5.3.20 Diisopropyl fluorophosphate

CAS No. 55-91-4

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Kilpatrick and Kilpatrick (1) have reported the acid, neutral, and base hydrolysis rate constants as 3.8 M^{-1} hr^{-1}, 7.2 X 10^{-3} hr^{-1} and 27.6 M^{-1} hr^{-1}, respectively at 25°C.

1. Kilpatrick, M. and M. L. Kilpatrick. 1949. The Hydrolysis of Diisopropyl Fluophosphate. J. Phys. Colloid. Chem. 53, 1371-1384.

5.3.21 Dimethoate

CAS No. 60-51-5

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

The rate constant for neutral hydrolysis at 25°C is 1.72×10^{-4} hr^{-1} with an alkaline second-order rate constant of 756 M^{-1} hr^{-1}. The reported rate and half-life were extracted from Grimmer et. al. (1) who measured the rates of hydrolysis of several phosphate esters at 25°C and 40°C and from pH 2 to 10.

1. Grimmer, F., W. Dedek and E. Leibnitz. 1968. I. Mitt. Hydrolysegeschwindigkeit Und Mechanismus. Z. Naturforschg. 1968. B23(1), 10-17

5.3.22 2,4-Dithiobiuret

CAS No. 541-53-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
3.07	85	0.52		1.2	0.999
3.08	85	0.56		1.4	0.841
3.03	65	0.08		8.7	0.990
7.12	85	1.13		0.7	0.922
7.12	85	1.33		0.5	0.944
7.04	65	0.26		2.6	0.976
7.04	65	0.26		2.6	0.943
9.60	85	1.12		0.7	0.887
9.60	85	0.84		0.7	0.996
9.99	65	0.24		2.9	0.861

Comments: Rate data at pH 7 and 9 were used to calculate a neutral energy of activation and log A (E_a = 17,814 ± 3561 cals/mole, log A = 10.92 ± 1.51). Hydrolysis was retarded at lower pH.

Water Solubility:

Source: Pfaltz and Bauer

Listed Purity: identity-purity confirmed by spectral analysis.

Analysis Concentration: 7 mg/L in H_2O/buffer

Analytical Procedure: Direct injection - 20 ml onto LC

Instrumentation: GC ___ HPLC X

Detector: UV - 280 nm

Column: Ultrasphere ODS, 5 micron, 4.6mm X 25cm

Mobile Phase: Acetonitrile: 0.05 M, NaH_2PO_4 (5:95)

5.3.22 2,4-Dithiobiuret

$K_1 = 1.3\ hr^{-1}$
$T_{1/2} = 0.5\ hr$
$R^2 = 0.944$

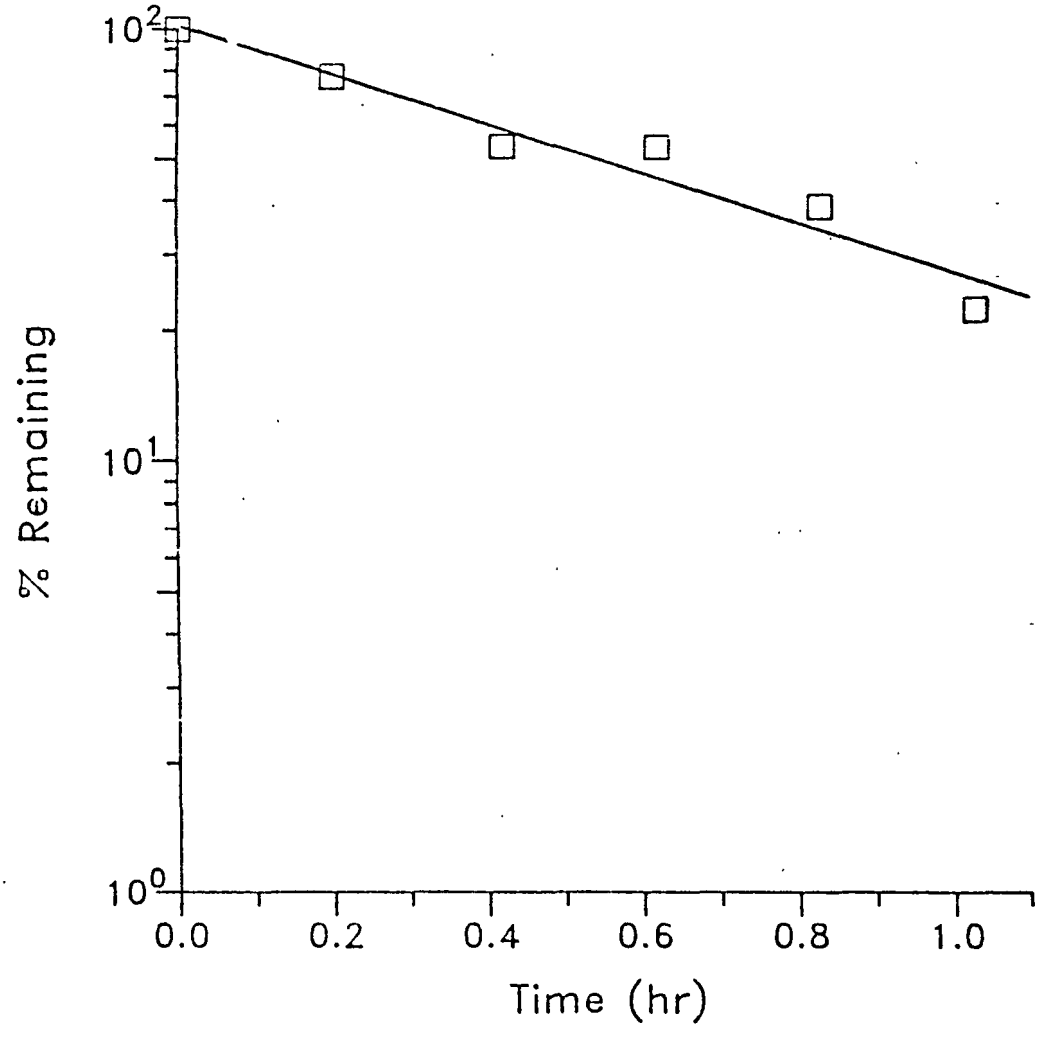

Figure 5.3.22 Hydrolysis of 2,4-Dithiobiuret at 85°C, pH 7.12

5.3.23 Ethyl methanesulfonate

CAS No. 62-50-0

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Barnard and Robertson (1) reported an activation energy of 21,120 cals/mole and neutral hydrolysis rate constant of 0.015 hr^{-1} at 25°C.

1. Barnard, P. W. C. and R. E. Robertson. 1961. The Hydrolysis of a Series of Straight-Chain Alkyl Methanesulphonic Esters in Water. Can. J. Chem. 39, 881-888.

5.3.24 Ethylene thiourea

CAS No. 96-45-7

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Ethylene thiourea (ETU) is very stable toward hydrolysis. No changes in concentration were observed in buffered aqueous solutions (pH 5, 7, and 9) held at 90°C for 3 months (1). ETU is a decomposition product of the dithiocarbamates such as Maneb and Nabam.

1. Cruickshank, P. A. and H. C. Jarrow. 1973. Ethylenethiourea Degradation. J. Agr. Food Chem. 21. 333-335.

5.3.25 Ethylene-Bis-(Dithiocarbamic Acid)*

CAS No. 11-54-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.15	45.5	5.45	7694	0.005	0.992
3.03	45.5	7.66	8214	0.004	0.999
2.96	29.0	1.48	1351	0.02	0.988
7.07	66.0	0.142		0.20	0.988
7.07	66.0	0.145		0.20	0.954
7.12	45.5	0.044		0.66	0.958
7.12	45.5	0.054		0.54	0.886
9.95	66.0	0.358		0.08	0.973
10.13	66.0	0.507		0.06	0.954
10.55	45.5	0.224		0.13	0.978
10.55	45.5	0.211		0.14	0.955

*The free acid is unstable; chemical analyzed was the disodium salt (Nabam).

Comments: Metal salts of ethylene-bis-dithiocarbamic acids can follow at least two routes of decomposition. Route 1, favored by boiling dilute acid, yields transient formation of the free acid with immediate decomposition to two moles of carbon disulfide and 1 mole ethylenediamine. Route 2 is a slower reaction favored by cooler dilute acid. Route 2 yields 1 mole of ethylenethiourea, 1 mole of carbon disulfide and 1 mole of hydrolgen sulfide (1).

1. Clarke, D. B., H. Baum, E. L. Stanley and W. F Hester. 1951. Determination of Dithiocarbamates, 23 1842-1850.

Water Soluoility: > 1.0 g/L

Source: RTP

Analysis Concentration: 10 mg/L

Analytical Procedure: Read on UV spectrophotometer - maxima at 286-90 nm

Instrumentation: Diode Array UV

5.3.25 Ethylene–bis(dithiocarbamic acid), sodium salt

$K_1 = 7.7\ hr^{-1}$
$T_{1/2} = .09\ hr$
$R^2 = 0.999$

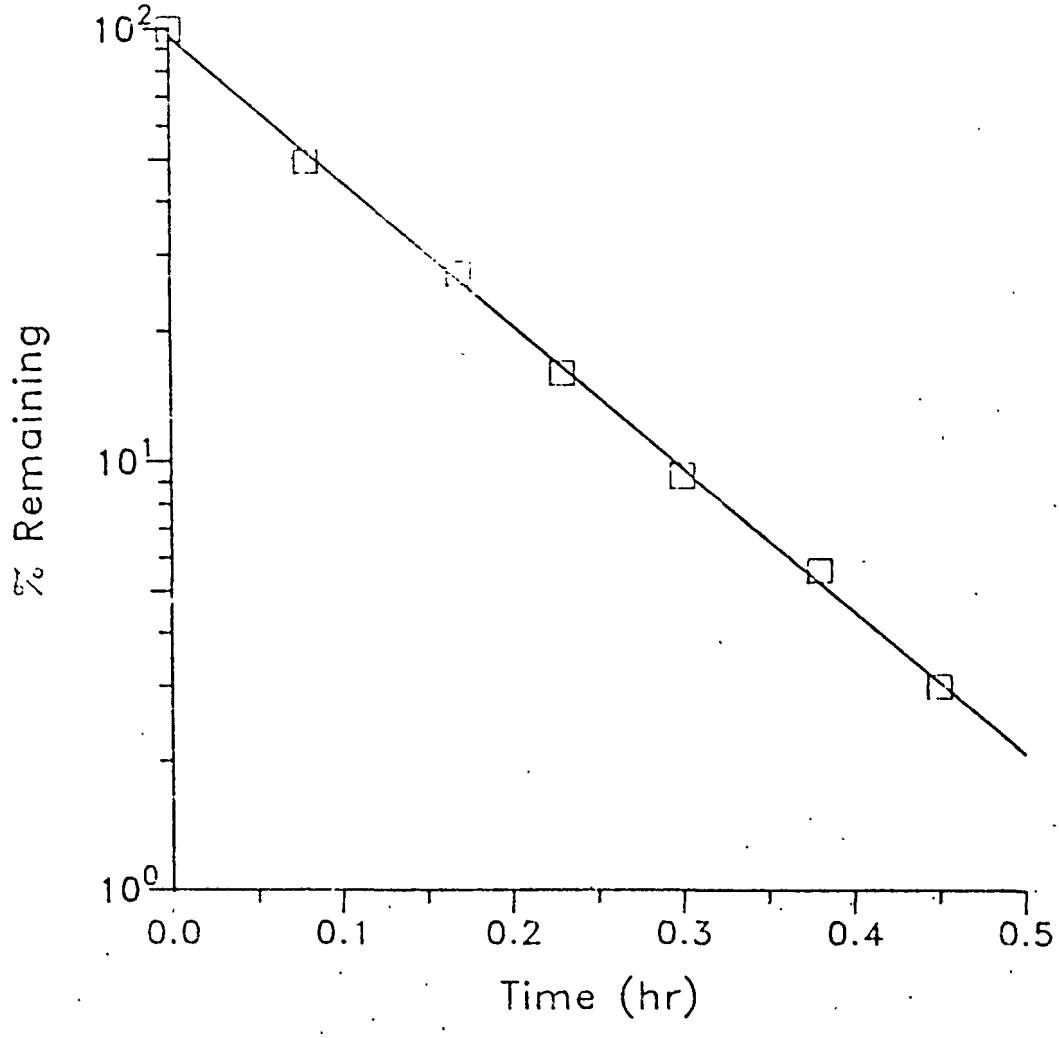

Figure 5.3.25 Hydrolysis of Ethylene–bis(dithiocarbar acid), sodium salt at 45.5°C, pH 3.03

5.3.26 2-Fluoroacetamide

CAS No. 640-19-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
3.02	85.5	0.011		63.0	0.998
3.02	85.5	0.011		63.0	0.997
7.23	85.5	0.011		63.0	0.998
7.23	85.5	0.012		58.0	0.999
7.04	85.5	0.009		77.0	0.997
7.04	85.5	0.009		77.0	0.998
9.66	85.5	0.802	545	0.9	0.999
9.66	85.5	0.661	449	1.0	0.999
9.66	85.5	0.863	587	0.8	0.985
9.75	85.5	0.946	523	0.7	0.985
10.41	69.2	1.51	382	0.5	0.997
10.41	69.2	1.54	389	0.5	0.998
10.41	69.2	1.59	402	0.4	0.997

Comments: The calculated alkaline activation energy is 4,436 ± 3,333 cals/mole, and the log A is 5.43 ± 1.88. The pH 3 and pH7 data were used to calculate the hydrolysis rate and half-life at pH 7 and 25°C.

Water Solubility: "Freely" Merck No. 4051 Ninth ed.

Source: Aldrich

Listed Purity: 98% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 6 ppm

Analytical Procedure: Direct aqueous injections;

Instrumentation: GC X HPLC ___

Detector: FID at 200°C

Column: DBWAX, 30m x 0.53mm ID

Temperature Program: 95°C to 150°C for 1.2 min at 15°C per min

5.3.26 2-Fluoroacetamide

$K_1 = 1.2 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 2.4$ days
$R^2 = 0.999$

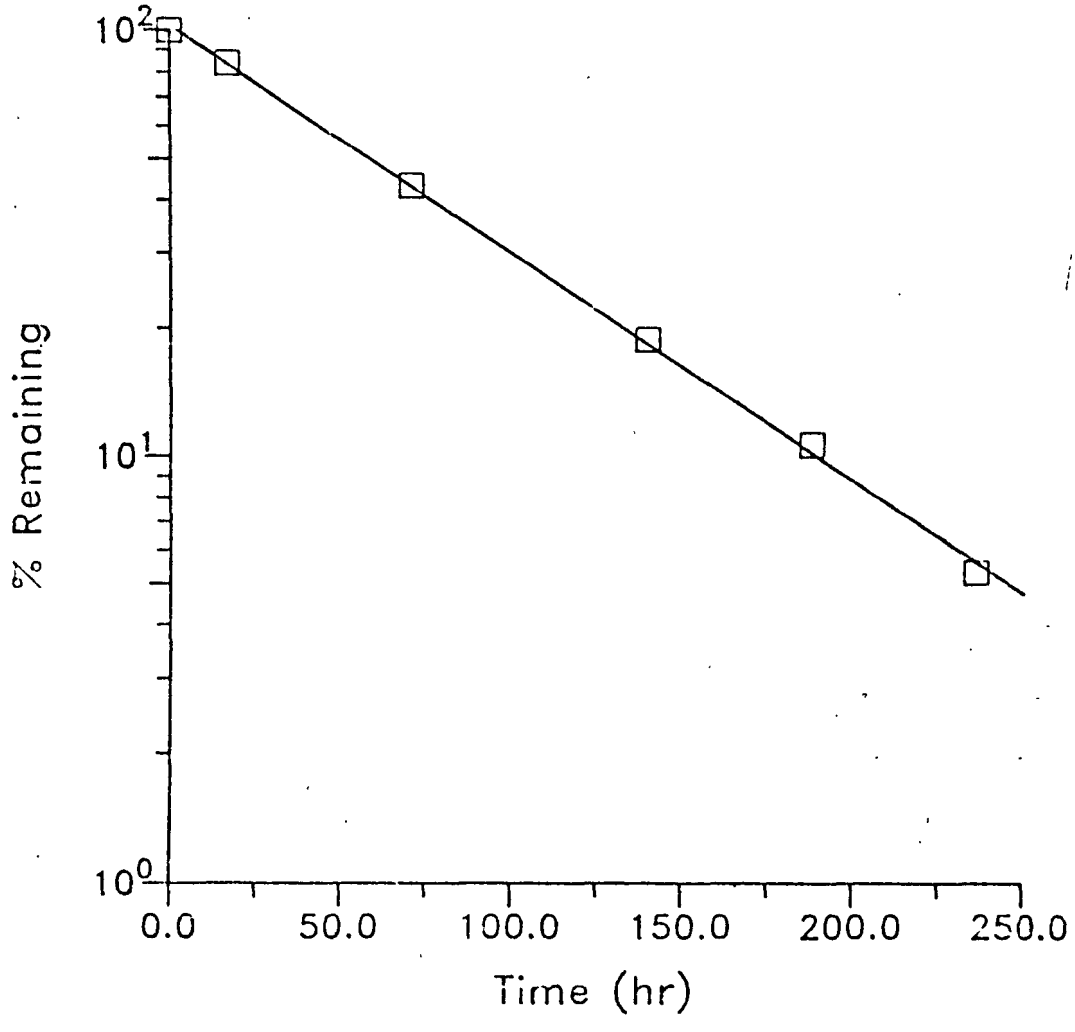

Figure 5.3.26 Hydrolysis of 2-Fluoroacetamide at 85.5°C, pH 7.23

5.3.27 Hexachlorobenzene

CAS No. 118-74-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	
3.13	85	
3.13	85	
3.13	85	
7.20	85	No detectable disappearance within experimental error
7.20	85	after 13 days at 85°C.
7.20	85	
9.27	85	
9.27	85	
9.27	85	

Water Solubility:

Source: RTP

Listed Purity: 98 - 99% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 5 µg/L in buffered water

Analytical Procedure: Extract 10 ml buffer with 2 ml of 250 µg/L 2,4-D methyl ester in isooctane. Inject isooctane layer with a final concentration of 25 µg/L hexachlorobenzene and 250 µg/L 2,4-D methyl ester as the internal standard.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: DB-5, 1.0 micron film, 15m x 0.53mm ID

Temperature Program: 180°C isothermal

Internal Standard: 250 µg/L 2,4-D methyl ester

5.3.28 Hexachloroethane

CAS No. 67-72-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	
3.10	85	
3.16	85	
3.16	80	
7.16	85	No detectable disappearance within experimental error after 11 days.
7.18	85	
7.18	85	
9.36	85	
9.65	85	
9.65	85	

Water Solubility:

Source: RTP

Listed Purity: 98% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 0.6 mg/L

Analytical Procedure: Extract 10 ml buffer with 2 ml of 7.77 mg/L solution of 1,2,4-trichlorobenzene in isooctane. Dilute 1:600 with isooctane for a final GC analysis concentration of 5 µg/L.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: OV-1, 5m x 0.53 mm, 2.65 micron

Temperature Program: 80°C for 4.5 min to 200°C at 70°C per min

Internal Standard 1,2,4-trichlorobenzene

5.3.29 Hexaethyl tetraphosphate

CAS No. 757-58-4

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

The stability of hexaethyl tetraphosphate to hydrolysis is the same as tetraethyl pyrophosphate: $k_1 = 0.093\ hr^{-1}$ and half-life 7.5 hr at 25°C and pH 7 (1).

1. Coates, H. 1949. The Chemistry of Phosphorus Insecticides. Am. Appl. Biol. 36, 156-159.

5.3.30 Isodrin

CAS No. 465-73-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp. °C	$X10^3 k_1 (hr^{-1})$	$k_2 (M^{-1}hr^{-1})$	$t_{1/2}$ (d)	r^2
3.47	84	<.5		>55	-----
3.47	84	0.6		48	0.690
3.47	84	<.5		>55	-----
7.32	84	0.5		58	0.667
7.32	84	0.9		32	0.531
9.73	84	<.5		>55	-----
9.73	84	<.5		>55	-----
9.73	84	<.5		>55	-----

Comments: Half-life was calculated from estimated 10% disappearance after nine days.

Water Solubility:

Source: Aldrich

Listed Purity: 98% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 5 µg/L

Analytical Procedure: Isodrin concentrations were 5 ppb in buffered water during kinetic measurements. Extraction of a 10-ml sample with 2 ml of isooctane that contained endosulfan I (28 ppb) and dilution of the extract with 2-ml isooctane gave a GC analysis concentration of 12.5 µg/L

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: OV-1, 2.65 micron film, 5m x 0.53mm ID

Temperature Program: 190°C isothermal

Internal Standard: Endosulfan I

5.3.31 Lasiocarpine

CAS No. 303-34-4

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.16	85	<.0006		>48.0	-----
3.16	85	0.0006		>48.0	-----
3.16	85	0.0006		>48.0	-----
7.08	85	0.015		1.9	0.964
7.08	85	0.014		2.0	0.993
7.08	85	0.014		2.0	0.991
9.50	85	1.10	1099	0.03	0.990
9.50	85	1.22	1225	0.02	0.997
9.50	85	1.16	1167	0.02	0.988
9.85	65	0.25	281	0.12	0.992
9.85	65	0.25	291	0.12	0.997

Comments: The calculated energy of activation for the base catalyzed hydrolysis is E_a = 16,866 ± 846 cals/mole with log A 13.4 ± 0.10.

Water Solubility:

Source: RTP

Listed Purity: 62% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 4 ppm

Analytical Procedure: Lasiocarpine was analyzed by direct injection of 20 microliters of each sample onto the column.

Instrumentation: GC ___ HPLC X

Detector: UV at 230 nm

Column: Nova Pak C_{18}

Mobile Phase: acetonitrile:water (50:50) with .005 M Pic B 8

5.3.31 Lasiocarpine

$K_1 = 1.4 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 2$ days
$R^2 = 0.991$

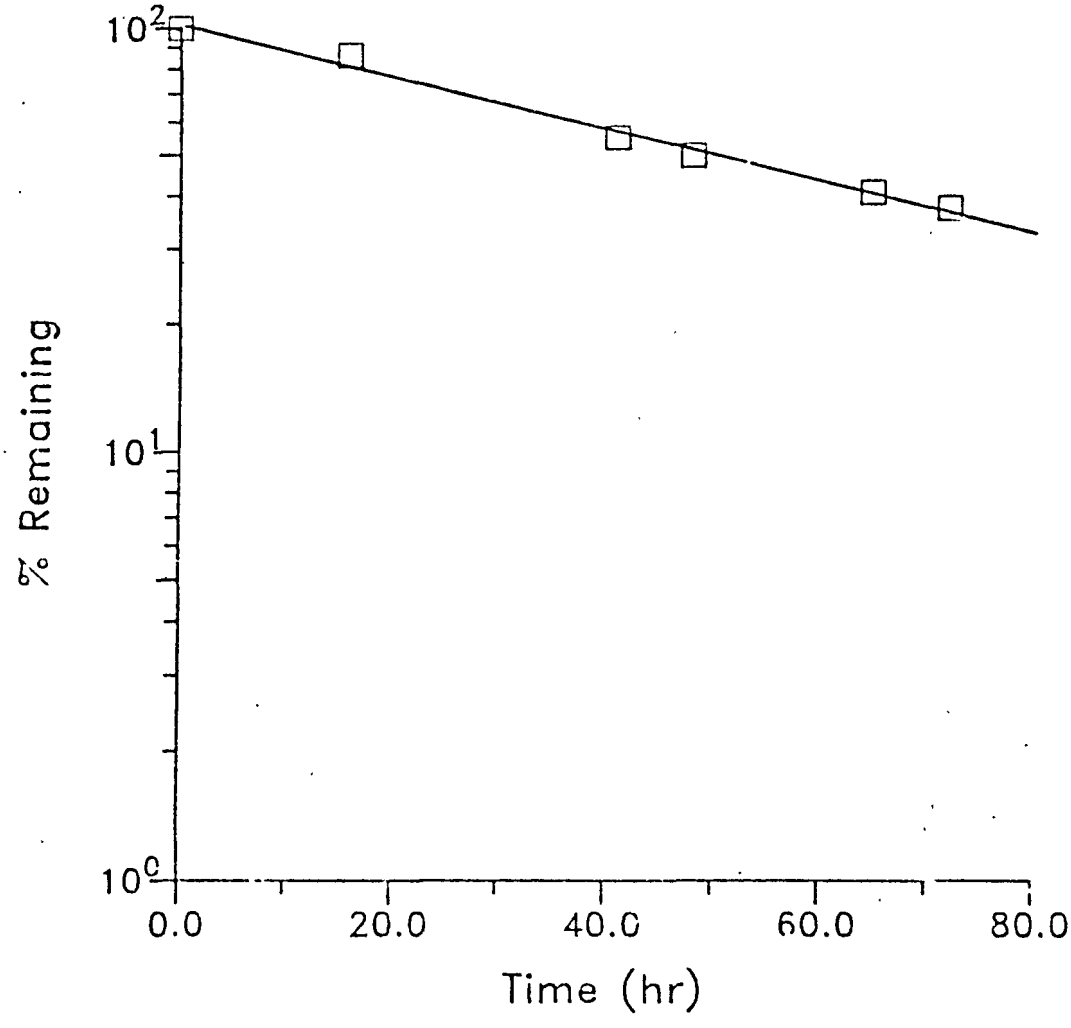

Figure 5.3.31 Hydrolysis of Lasiocarpine at 85°C pH 7.08

5.3.32 Lindane

CAS No. 58-89-9

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.,°C	$X10^3 k_1$ (hr^{-1})	k_2 ($M^{-1}hr^{-1}$)	$t_{1/2}$	r^2
2.96	65.5	0.4		65 d	0.251
2.99	84.4	1.4		20 d	0.894
2.99	84.4	1.0		29 d	0.651
2.99	84.4	0.7		43 d	0.320
3.17	65.5	<.1		>300 d	------
3.17	65.5	0.1		240 d	0.517
3.17	65.5	0.3		107 d	0.377
6.85	65.5	6.5		4.4 d	0.996
7.24	65.5	12.0		2.4 d	0.999
7.24	65.5	12.2		2.4 d	0.997
7.24	65.5	11.9		2.4 d	0.999
10.98	46.0	4290	1056	0.16 h	0.999
10.98	46.0	4680	1152	0.15 h	0.997
11.08	46.0	5000	978	0.14 h	0.994
11.29	37.0	2410	552	0.03 h	0.999
11.60	23.0	595	174	1.15 h	0.980

Comments: The calculated energy of activation for base catalyzed hydrolysis is: E_a = 15,100 + 500 cals/mole, log A = 13.09 + 0.18.

Water Solubility: 6-12 mg/L

Source: RTP

Listed Purity: 95% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 200 µg/L

Analytical Procedure: Extract 10 ml buffer with 2 ml of 5.2 mg/L 2,4-D methyl ester in isooctane. Dilute 1:100 with isooctane for a final analysis concentration of 20 µg/L lindane and 100 µg/L I.S.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: OV-1, 2.65 micron film, 5m x 0.53mm

Temperature Program: 160°C isothermal

Internal Standard: 2,4-D methyl ester

5.3.32 Lindane

$K_1 = 2.4\ hr^{-1}$
$T_{1/2} = 0.3\ hr$
$R^2 = 0.999$

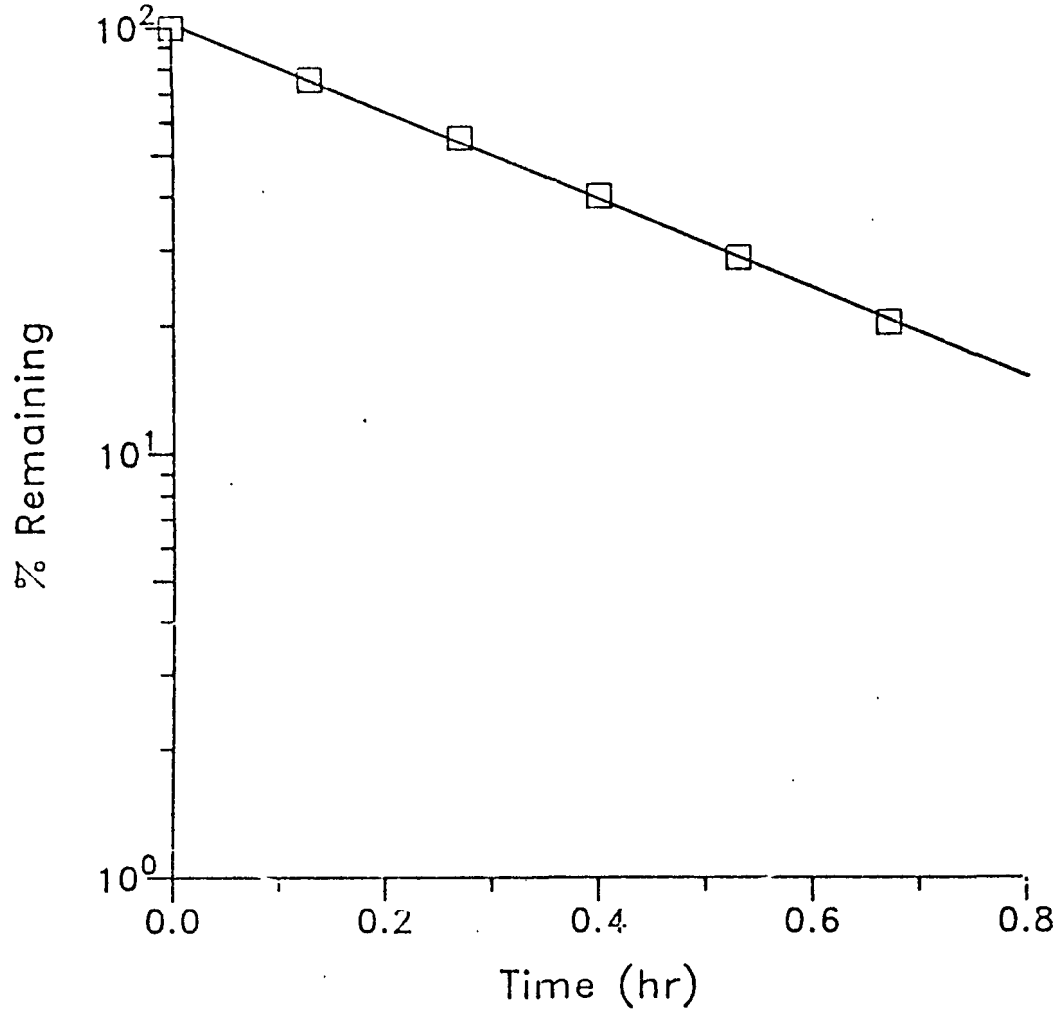

Figure 5.3.32 Hydrolysis of Lindane at 37°C pH 11.29

5.3.33 Malononitrile

CAS No. 109-77-3

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$10^3 k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
3.24	85.5	5.0		139	0.923
3.31	85.6	1.6		433	0.911
3.31	85.6	0.8		866	0.810
7.09	85.5	288.0		2.4	0.982
7.21	85.5	510.0		1.4	0.994
7.21	85.5	456.0		1.5	0.990
7.21	85.5	588.0		1.2	0.985
7.14	85.6	288.0		2.4	0.998
8.85	27.0	8.8	1067	78.8	0.983
8.97	27.5	11.4	1010	60.8	0.992
8.97	27.5	11.8	1046	58.7	0.986
8.97	27.5	13.0	1152	53.3	0.987

Comments: Extrapolated alkaline second-order rate constant to 25°C was 806 ± 45 M^{-1} hr^{-1} (assumed E_a = 20, cals/mole).

Water Solubility: 13 g/100 ml 1300 mg/L

Source: Aldrich

Listed Purity: 99%

Analysis Concentration: 25 mg/L

Analytical Procedure: Basic runs were neutralized with 8 drops of 0.5 M NAH_2PO_4

Instrumentation: GC X HPLC ___

Detector: FID

Column: DBWax 30m .53mm ID 1.0 micron film

Temperature Program: 95°C then 40°C/min to 160°C

Internal Standard: 3-chloropropanenitrile

5.3.33 Malononitrile

$K_1 = 5.1 \times 10^{-1}\ hr^{-1}$
$T_{1/2} = 1.4\ hr$
$R^2 = 0.995$

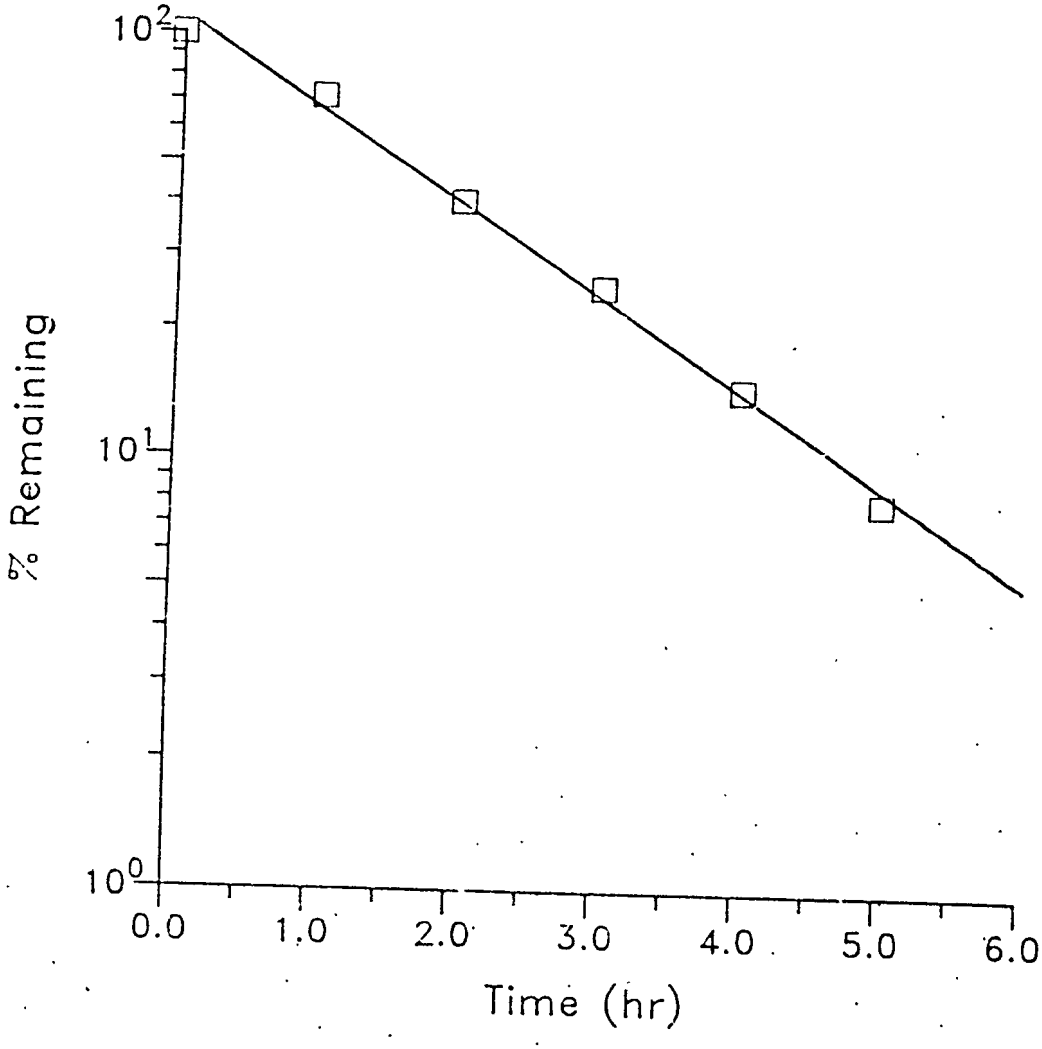

Figure 5.3.33 Hydrolysis of Malononitrile at 23.8°C pH 7.13

Internal Standard: 2,4-D methyl ester

5.3.34 Melphalan

CAS No. 148-82-3

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Melphalan is a nitrogen mustard used in cancer chemotherapy. Melphalan hydrolysis is not acid or base catalyzed. The neutral hydrolysis rate at 25°C is: $k = 0.146\ hr^{-1}$ and half-life of 4.8 hours (1).

1. Flora, K. P., S. L. Smith and J.C. Cradock. 1979. Application of a Simple High-Performance Liquid Chromatographic Method for the Determination of Melphalan in the Presence of its Hydrolysis Products. J. Chromatogr. 177, 91-97.

5.3.35 Methomyl

CAS No. 16752-77-5

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Chapman and Cole (1) reported the pH-disappearance rate profile at 25°C for methomyl at pHs 4.5, 6, 7, and 8 in sterile phosphate buffers. No catalysis by acid was observed. A neutral rate constant (8.9×10^{-5} hr^{-1}) and an alkaline second-order constant (210 M^{-1} hr^{-1}) was calculated. The second-order constant was in good agreement with Lemley and Zhong (258 M^{-1} hr^{1}, 25°C, 79.2 M^{-1} h^{-1} at 15°C).

1. Chapman, R. A. and C. M. Cole. 1982. Observations on the Influence of Water and Soil pH on the Persistence of Insecticides, J. Environ. Sci. Health. B17(5), 487-504.

2. Lemley, A. T., W. Z. Zhong, G. E. Janauer and R. Rossi. 1984. Chapter 15 in Treatment and Disposal of Pesticide Wastes, R. F. Kruger and J. N. Seiber Eds., ACS Symposium Series, Washington, D.C. pp. 245- 259.

5.3.36 Methyl methacrylate

CAS No. 80-62-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$10^3 k_1 (hr^{-1})$	$k_2 (M^{-1}hr^{-1})$	$t_{1/2}$(hr)	r^2
3.17	85.0	No measureable hydrolysis, 53 hr			
3.17	85.0	No measureable hydrolysis, 53 hr			
7.07	25.0	No measureable hydrolysis, 72 hr			
7.11	85.0	0.1860		3.7	0.804
7.11	85.1	0.0078		88.4	0.789
7.11	85.1	0.0187		37.1	0.977
9.33	85.5	Complete hydrolysis, 15 min			
9.86	66.0	1.84	1940	0.37	0.993
10.00	66.2	4.60	3480	0.15	0.999
10.06	66.5	4.04	2620	0.17	0.990
11.13	25.0	0.31	230	2.23	0.995
11.13	25.0	0.26	190	2.66	0.981
11.13	25.0	0.24	180	2.88	0.977

Comments: The hydrolysis at pH 7 can be attributed to hydroxide catalysis. The second-order alkaline hydrolysis rate constant at 25°C (200 ± 47 M^{-1} hr^{-1}, α= 0.05) is in good agreement with Shrama and Shrama (1) [171 M^{-1}_1 hr^{-1}].

Water Solubility: "Sparingly" JARC Vol 19 (1979)

Source: Aldrich

Listed Purity: 99% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 10.5 ppm

Analytical Procedure: Prepared fresh stock prior to each run in autoclaved H_2O. Added to buffer for an initial analysis concentration of 10.5 ppm direct aqueous injection.

Instrumentation: GC X HPLC ___

Detector: FID

Column: DBWax 30m, 0.53mm ID

5.3.37 N-Methyl-N-Nitro-N-Nitrosoguanidine

CAS No. 70-25-7

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Hydrolysis is catalyzed by hydronium ion below pH 3 (k_{acid} = 4.9 $M^{-1}hr^{-1}$, 25°C). It has a second-order alkaline hydrolysis rate constant of approximately 9.5 X 10^4 M^{-1} hr^{-1} at 25°C (1). The observed half-life at pH 7 and 37°C was 5 hours. The above yields a neutral rate of 0.027 hr^{-1} at 25°C.

1. McCalla, D. R., A. Reuvers and R. Kitai. 1968. Inactivation of Biologically Active N-Methyl-N-Nitro-N-Nitroso Compounds in Aqueous Solution: Effect of Various Conditions of pH and Illumniation. Canad. J. Biochem. 48, 807-811.

5.3.38 2-Methylaziridine

CAS No. 75-55-8

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Water is sufficiently acidic to provide a very low concentration of 2-methylaziridinium ion (approx. 2×10^{-5}) (1). The iminium ion has a pK_a of 9.61 and the free imine has a pK_b of 5.38 (1). The rate constant for a ring opening in aqueous solutions was $(7.0 \pm 0.2) \times 10^{-3}$ min^{-1} at 65°C. The derived rate and half-life at 25°C are 0.008 hr^{-1} and 87 hr, respectively. Addition of acids accelerates production of the aminoalcohols and/or polymerization. Bunnett et al. (2) reported data that yields an acidic second-order rate constant of 4.0×10^{-3} M^{-1} hr^{-1}.

1. Biust, G. J., and H. J. Lucas. 1957. Basicity Constants and Rates of Hydration of Some Imines. J. Am. Chem. Soc. 79, 6157-6160.

2. Bunnett, J. F., R. L. McDonald And F. P. Olsen. 1974. Kinetics of Hydrolysis of Aziridines in Moderately Concentrated Mineral Acids. J. Am. Chem. Soc. 96, 1855-1861.

5.5.39 Methylthiouracil

CAS No. 56-04-2

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$10^3 k_1 (hr^{-1})$	$k_2 (M^{-1}hr^{-1})$	$t_{1/2}$(hr)	r^2
3.41	85	No hydrolysis after 8 days			
3.41	85	"	"		
3.41	85	"	"		
3.02	66	"	"		
5.72	85	1.07		27.0 d	0.898
5.72	85	0.69		42.0 d	0.647
5.72	85	0.54		54.0 d	0.915
7.17	66	7.6		3.8 d	0.847
7.35	85	91.5		0.3 d	0.848
7.35	85	95.5		0.3 d	0.932
7.35	85	75.4		0.4 d	0.991
9.05	66	13.7		2.1 d	0.847
9.65	85	27.3		1.1 d	0.990
9.65	85	37.4		0.8 d	0.837
9.65	85	34.3		0.8 d	0.896

Comments: At pH 7.35 and 85°C the hydrolysis rate is three times greater than the rate at pH 9.65 and 85°C (pH was measured at 85°C). 6-Methyl-3-thiouracil has two ionizable protons and hence two pKs. Thus the ionization can be written as:

$$H_2A \underset{7.73}{\overset{pK_1}{\rightleftharpoons}} HA^- \overset{Pk_2}{\rightleftharpoons} A^{2-}$$

where a value of 7.33 (1) has been reported for pK_1. The value of pK_2 would be >11. The resistance to acid hydrolysis and the greater rate of hydrolysis at pH 7.35 is strong evidence that the monoion (HA^-) is the degraded species. Hydrolysis is most likely mediated by attack of a molecule of water on the

monoanion. As the pH is increased, the equilibrium is shifted more to the dianion and the rate of hydrolysis correspondingly decreases. Thus the rate at pH 7.35 and 85°C was extrapolated to pH 7 and 25°C using the calculated E_a = 32,649 cals/mole.

1. Garret, E. R., and D. J. Weber. 1970. Metal Complexes of Thiouracils I: Stability Constants by Potentiometric Titration Studies and Structures of Complexes. J. Pharm. Sci. 59, 1383-1398.

Water Solubility: 0.48 g/L

Source: Aldrich

Listed Purity: 99% Identity-purity was confirmed by spectral analysis

Analysis Concentration: 1.1 ppm in buffered H_2O

Analytical Procedure: 20 ml direct injection on LC

Instrumentation: GC ___ HPLC X

Detector: UV - 280 nm

Column: Waters Nova-Pak C_{18} (4 M, 4.6mm X 15cm)

Mobile Phase: 0.05 M NaH_2PO_4:Methanol (90:10)

5.3.39 Methylthiouracil

$K_1 = 1.4 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 2.1$ days
$R^2 = 0.937$

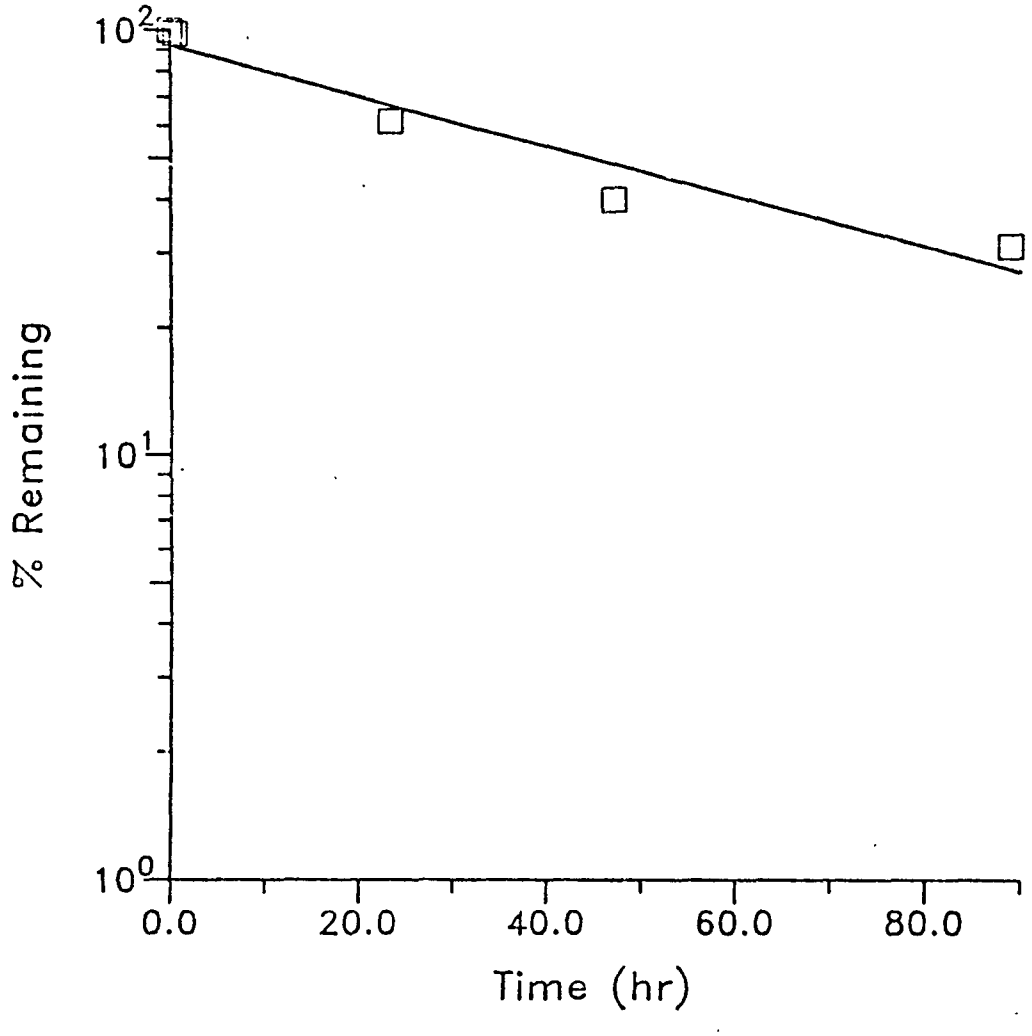

Figure 5.3.39 Hydrolysis of Methylthiouracil at 66°C, pH 9.05

5.3.40 Alpha-Naphthylthiourea

CAS No. 86-88-4

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.26	85	0.009		3.1	0.995
3.26	85	0.010		2.8	0.964
3.26	85	0.011		2.6	0.972
7.17	85	0.019		1.5	0.915
7.17	85	0.025		1.2	0.988
7.17	85	0.024		1.2	0.985
9.80	85	0.046	25.0	0.6	0.944
9.80	85	0.049	27.0	0.6	0.981
9.80	85	0.056	31.0	0.5	0.964

Water Solubility:

Source: RTP

Listed Purity: 93.9% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 2 mg/L

Analytical Procedure: Alpha-Naphthaylthiourea was analyzed by direct injection of 20 microliters buffered solution onto the Resolvex C_{18} column for each sample.

Instrumentation: GC ___ HPLC X

Detector: UV at 222 nm

Column: Resolvex C_{18}, 10 micron, 4.6 x 25cm

Mobile Phase: acetonitrile:water (50:50)

5.3.40 Alpha–Naphthylthiourea

$K_1 = 2.5 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 1.2$ days
$R^2 = 0.988$

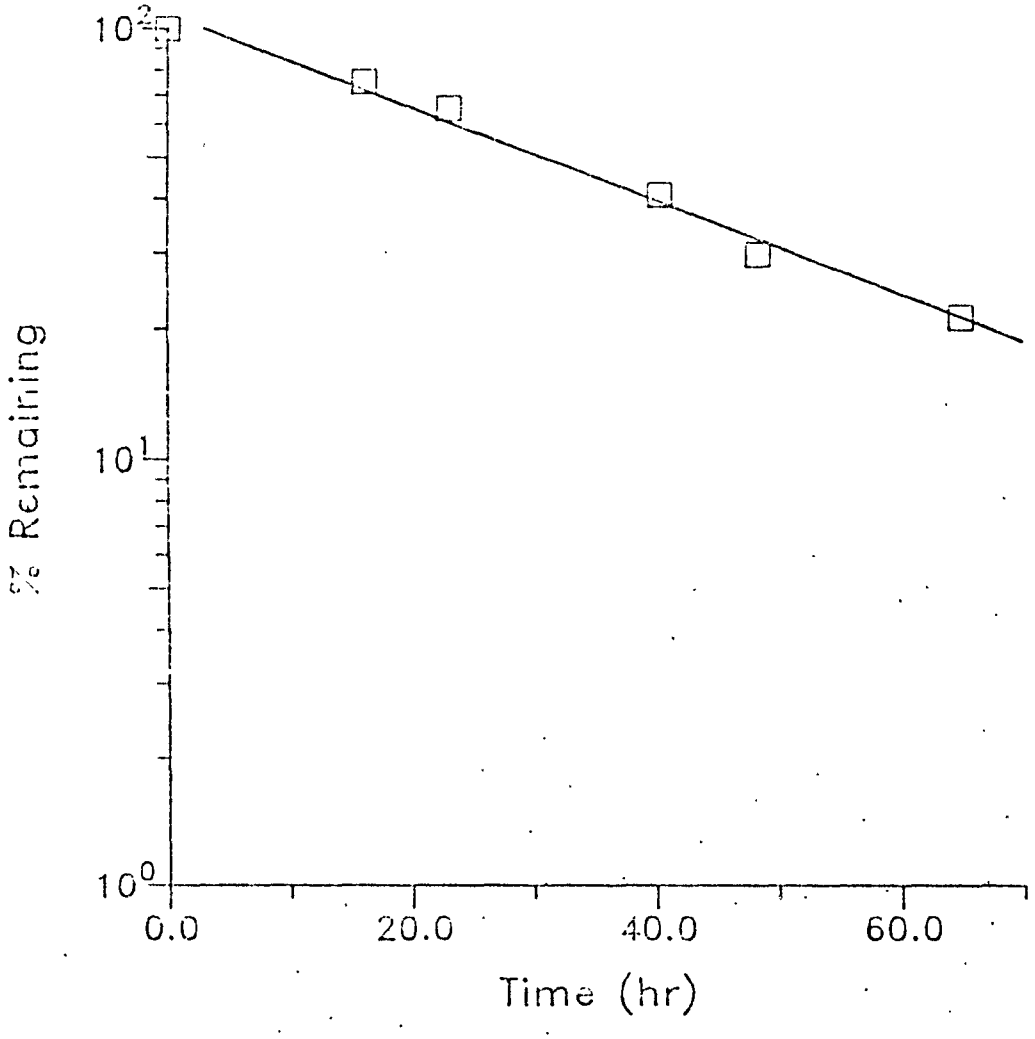

Figure 5.3.40 Hydrolysis of Alpha–Naphthyl thiourea at 85°C, pH 7.17

5.3.41 N-Nitroso-N-Ethylurea

CAS No. 759-73-9

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Druckrey et al. (1) reported stability data at 20°C and at pH values from 4 to 9. Values of second-order and neutral rate constants were extrapolated to 25°C. A half-life of 0.8 hours was calculated at 25°C and pH 7. This value was in good agreement with that of Garrett et al. (2).

1. Druckrey, H., R. Preussmann, S. Ivankovie and D. Schmahl. 1967. Orgontrope Carcinogene Wirkungen bei 65 Verschiedenen N-Nitroso-Verbindungen an BD-Ratten. Z. Krebforsch. 69, 103-201.

2. Garrett, E. R., S. Goto and J. F. Stubbins. 1965. Kinetics of Solvolyses of Various N-Alkyl-N-Nitrosoureas in Neutral and Alkaline Solutions. J. Pharm. Sci. 54, 119-123.

5.3.42 N-Nitroso-N-Methylurethane

CAS No. 615-53-2

HYDROLYSIS AND ANALYSIS DATA

Literature Data: Rate Data calcluated from McCalla et al. (1). McCalla reported rate data in one pH unit increments from pH 2 through pH 9 at 37°C.

1. McCalla, D. R., A. Reuvers and R. Kitai. 1968. Inactivation of Biologically Active N-Methyl-N-Nitroso Compounds in Aqueous Solution: Effects of Various Conditions of pH and Illumination. Canad. J. Biochem. 46, 807-811.

5.3.43 Octamethylpyrophosphoramide

CAS No. 152-16-9

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Heath and Cascipieri (1) measured the hydrolysis rates of some dimethylamides of phosphoric acids in acids, alkalies, and water. Octamethylpyrophosphoramide in water at pH 7 was held at 100°C for one week. No hydrolysis was observed within experimental error. The second-order acid and alkaline rate constants were 0.23 ± 0.03 M^{-1} hr^{-1} and 1 X 10^{-11} M^{-1} hr^{-1} respectively. The half-life at pH 7 and 25°C based on the acid contribution would be 3,400 years.

1. Heath, D. F., and P. Casapieri. 1950. Hydrolysis of Dimethylamides of Phosphoric Acids. Trans. Faraday Soc. 47, 1093-1101.

5.3.44 Di-n-Octylphthalate

CAS No. 117-84-0

HYDROLYSIS AND ANALYSIS DATA

Literature Data: Wolfe (1) et al. reported a second-order alkaline hydrolysis rate constant of 12.9 M^{-1} hr^{-1} at 30°C. Hydrolysis at neutral pH would be dominated by the alkaline contribution thus the calculated second-order rate at 25°C was used to determine the half-life at pH 7 and 25°C.

1. Wolfe, N. L., D. F. Paris, W. C. Steen and G. L. Baughman. 1980. Correlation of Microbial Degradation Rates with Chemicals Structure, Environ. Sci. Technol. 14, 1143-1144.

5.3.45 Phorate

CAS No. 298-02-2

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Chapman and Cole (1) determined at 25°C the pH-disappearance rate profiles for 24 insecticides including phorate. The determinations covered 4 or 5 pH values over the range 4.5 to 8 in sterile phosphate buffers. The neutral rate constant for phorate was 0.0072 hr^{-1} with a corresponding 96 hr half-life at 25°C. Acid or base catalysis was not observed in the above pH range.

1. Chapman, R. A., and C. M. Cole. 1982. Observations on the Influence of Water and Soil pH on the Persistence of Insecticides. J. Environ. Sci. Health. B17(5), 487-504.

5.3.46 1,3-Propane Sultone

CAS No. 1120-71-4

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

From the data of Bordwell et al. (1) a neutral hydrolysis rate constant of 0.082 hr^{-1} and half-life of 8.5 hr were calculated. The energy of activation was 20,400 cals/mole.

1. Bordwell, F. G., C. E. Osborne and R. D. Chapman. 1959. The Hydrolysis of Soltones. J. Am. Chem. Soc. 81, 2698-2705.

5.3.47 Safrole

CAS No. 94-59-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	
3.15	66.5	No detectable hydrolysis over 9 days
3.22	85.5	No detectable hydrolysis over 14 days
3.27	85.1	No detectable hydrolysis over 26 days
3.27	85.1	No detectable hydrolysis over 26 days
3.27	85.1	No detectable hydrolysis over 26 days
7.12	65.9	No detectable hydrolysis over 14 days
7.29	85.2	No detectable hydrolysis over 14 days
7.29	85.2	No detectable hydrolysis over 21 days
7.29	85.2	No detectable hydrolysis over 21 days
7.29	85.2	No detectable hydrolysis over 26 days
9.81	65.6	No detectable hydrolysis over 14 days
9.77	85.5	No detectable hydrolysis over 9 days
9.60	85.3	No detectable hydrolysis over 26 days
9.60	85.3	No detectable hydrolysis over 26 days
9.60	85.3	No detectable hydrolysis over 26 days

Water Solubility: Insoluble

Source: Aldrich

Listed Purity: 97% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 2.4 mg/L

Analytical Procedure: Safrole was analyzed by direct injections into a 20 microliter injection loop of each sample.

Instrumentation: GC ___ HPLC X

Detector: Kratos Spectroflow 757 UV at 290 nm

Column: ODS Ultrasphere 4.6mm x 15cm, 5 micron

Mobile Phase: methanol:water (65:35)

5.3.48 Tetraethyl pyrophosphate

CAS No. 107-49-3

HYDROLYSIS AND ANALYSIS DATA

Literature Data:

Tetraethyl pyrophosphate hydrolysis is a first-order reaction with a value of the rate constant of 0.093 hr^{-1} at 25°C and an activation energy of 10.7 Kcal/mole (1). The hydroxide catalyzed hydrolysis was too fast to measure.

1. Ketelaar, J. A. A. and A. H. Bloksma. 1948. The Rate of Hydrolysis and Composition of Tetraethyl pyrophosphate. Recueil. 67, 665-676.

5.3.49 Thioacetamide

CAS No. 62-55-5

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
7.18	85	0.025		1.2	0.923
7.18	85	0.026		1.1	0.847
7.18	85	0.020		0.9	0.925

Comments: Peters and De Ranter (1) reported an alkaline second-order rate constant of 4.55 ± 0.3 M^{-1} min^{-1} at 80°C (2.3 X 10^{-2} M^{-1} min^{-1} at 25°C) and an activation energy of 20,160 cal/mol. Swift and Butler (2) reported a second-order acid rate constant of 0.21 ± 0.023 M^{-1} min^{-1} at 90°C [(1 ± 0.01) X 10^{-3} at 25°C)] and an activation energy of 19,100 cals/mole. These values and the measured rate at pH 7.18 were used to derive a neutral hydrolysis rate constant of 1.43 X 10^{-6} min at 25°C.

1. Peeters, O. M. and C. J. De Ranter. 1976. Kinetics of the Hydrolysis of Thioacetamide in Alkaline Solution. J. Chem. Soc. (Perkin II), pp. 1062-1065.

2. Swift, E. H. and E. A. Butler. 1956. Precipitation of Sulfides from Homogeneous Solutions by Thioactamide. Anal. Chem. 28, 146-153.

Water Solubility: 16 g/100 ml

Source: Aldrich

Listed Purity: 99% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 2 mg/L in buffer

Analytical Procedure: 20 ml direct injection on HPLC

Instrumentation: GC ___ HPLC X

Detector: UV at 261 nm

Column: Ultrasphere ODS, 5 micron, (25cm X 4.6mm)

Mobile Phase: Actronitrile:water (50:50)

5.3.49 Thioacetamide

$K_1 = 1.8 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 1.6$ days
$R^2 = 0.930$

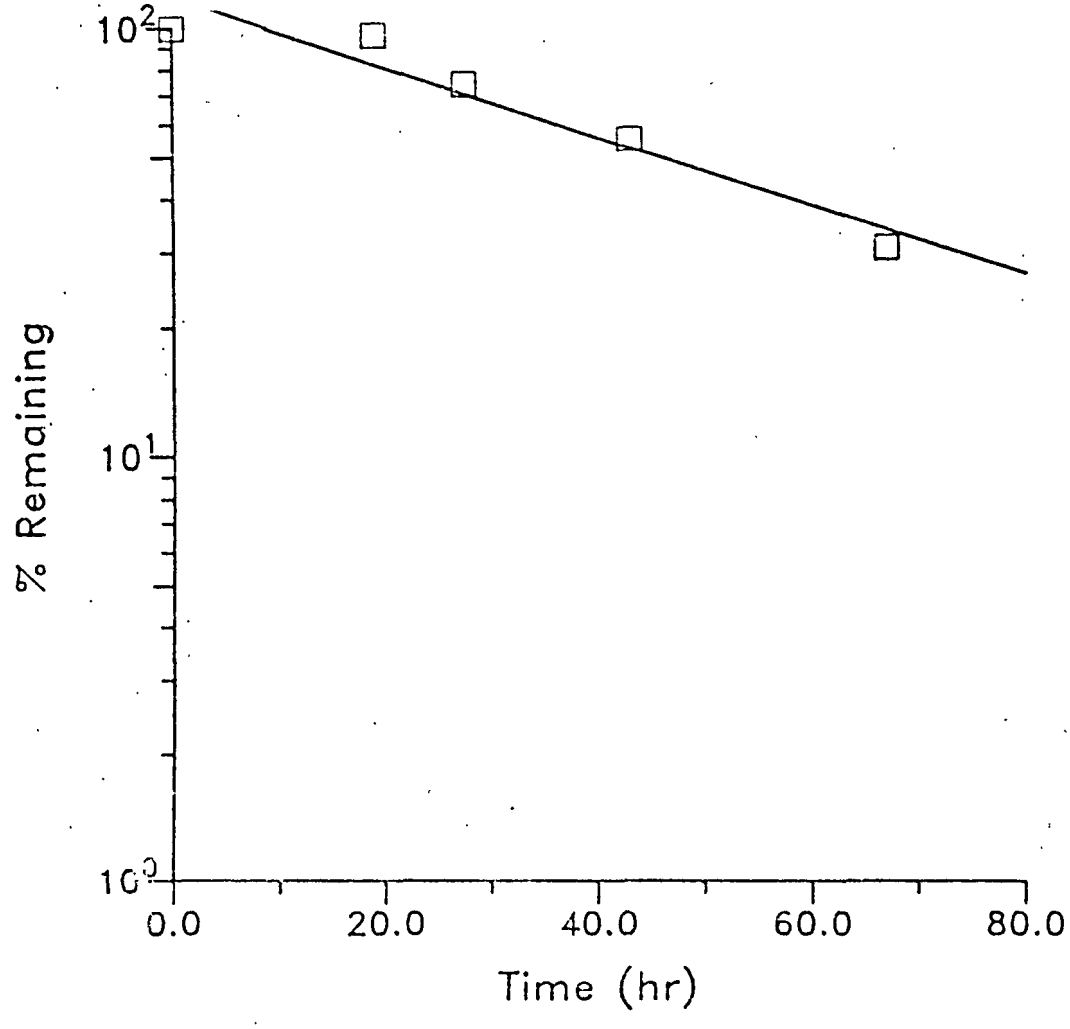

Figure 5.3.49 Hydrolysis of Thioacetamide at 85°C, pH 7.05

5.3.50 Thiram

CAS No. 137-26-8

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.22	85	0.06		0.49	0.999
3.29	85	0.06		0.49	0.963
6.96	65	0.27	$2.3x10^5$	0.11	0.995
6.97	65	0.26	$2.2x10^5$	0.11	0.993
6.97	65	0.29	$2.3x10^5$	0.11	0.998
10.49	24	1.83	6380	0.016	0.997
10.79	24	2.33	4070	0.012	0.978
10.79	24	2.26	3960	0.013	0.980

Water Solubility:

Source: RTP

Listed Purity: 99.5% Identity-purity confirmed by spectral analysis.

Analysis Concentration: 2 mg/L

Analytical Procedure: Thiram was analyzed by injection of 20 microliters onto an Ultrasphere ODS column for each sample.

Instrumentation: HPLC X

Detector: UV at 218 nm

Column: Ultrasphere ODS, 5 micron, 15 cm

Mobile Phase: acetonitrile:water (60:40)

5.3.50 Thiram

$K_1 = 1.8 \times hr^{-1}$
$T_{1/2} = 0.4$ hr
$R^2 = 0.997$

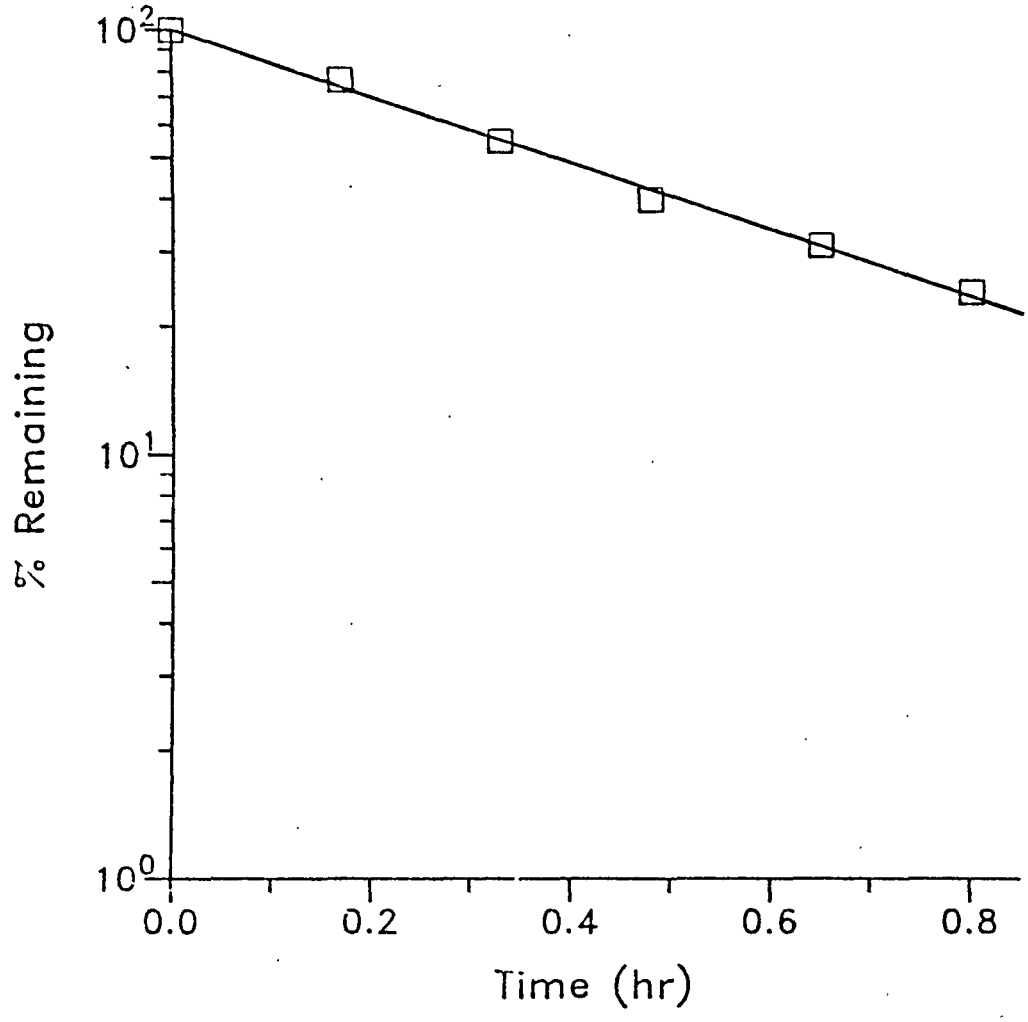

Figure 5.3.50 Hydrolysis of Thiram at 24°C, pH 10.49

5.3.51 Toxaphene

CAS No. 8001-35-2

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp. °C	$X10^3 k_1 (hr^{-1})$	$k_2 (M^{-1}hr^{-1})$	$t_{1/2}$(d)	r^2
3.24	85	3.0		9.8	0.980
3.25	85	2.0		14.4	0.804
3.25	85	1.8		15.9	0.920
7.20	85	5.6		5.2	0.956
7.20	85	4.1		7.0	0.562
7.20	85	4.7		6.2	0.894
9.63	85	2.0	0.7	1.6	0.974
9.35	85	10.5	3.7	2.7	0.603
9.35	85	15.2	5.2	1.9	0.965

Comments: Toxaphene is difficult to quantitate because it is a mixture of more than 670 compounds, primarily polychlorinated bornanes ($C_{10}H_{18-n}Cl_n$). The chlorine content is 67-69 percent by weight. Quantitation was based on decreasing response to electron capture detection for an envelope of GC eluted compounds. The hydrolysis values at pH 3 were used as the true neutral contribution to hydrolysis.

Water Solubility: 4 mg/L

Source: RTP

Listed Purity: 100% technical toxaphene, 68% chlorine. Identity-purity was confirmed by spectral analysis.

Analysis Concentration: 500 µg/L in buffered water

Analytical Procedure: Extract 10 ml buffer with 2 ml isooctane, dilute 1:25. Final analysis concentration was 100 µg/L.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: ECD

Column: OV-1, 2.65 micron film, 5m x 0.53mm ID

Temperature Program: 210°C isothermal

5.3.51 Toxaphene

$K_1 = 5.6 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 5.2$ days
$R^2 = 0.956$

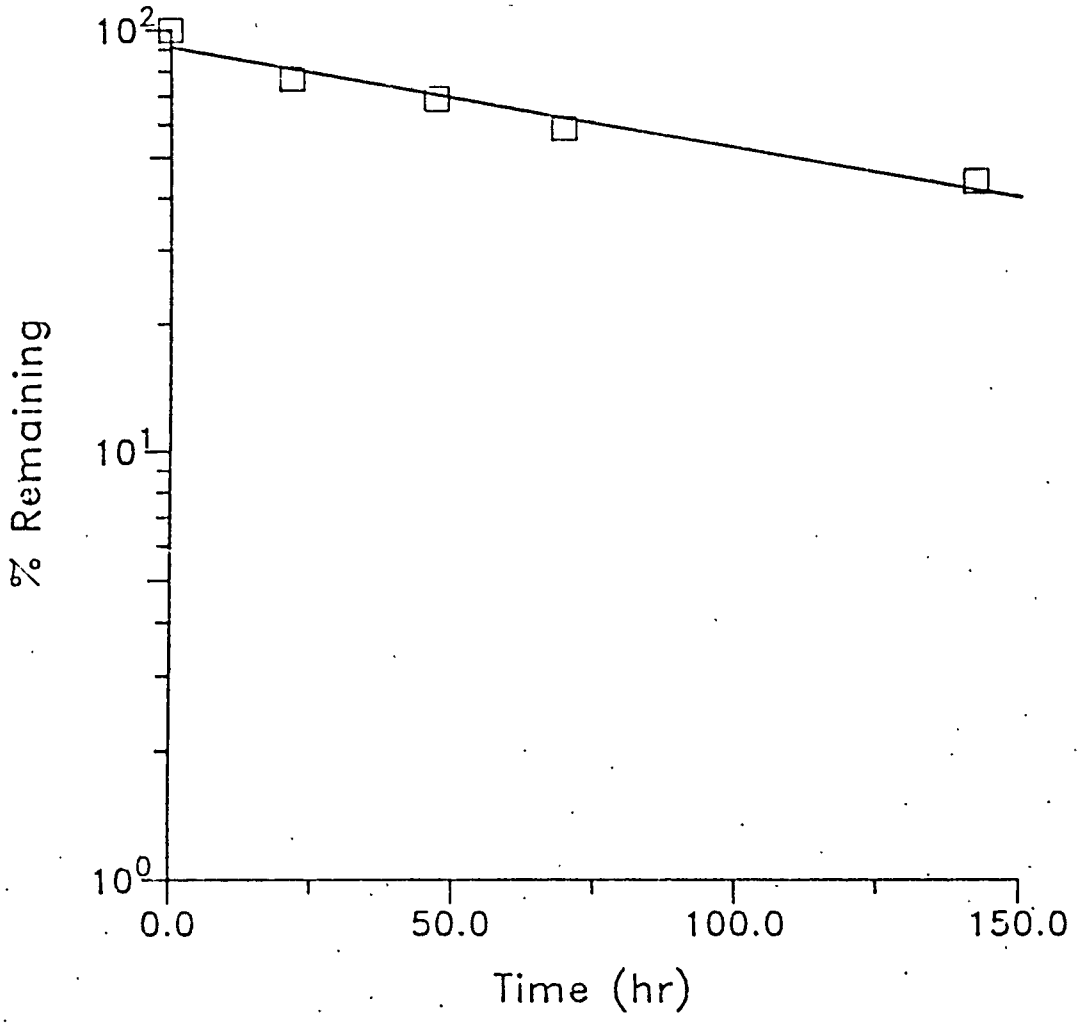

Figure 5.3.51 Hydrolysis of Toxaphene at 85°C, pH 7.20

5.3.52 0,0,0-Triethyl ester phosphorothioic acid

CAS No. 126-68-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$X10^3k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
3.09	85.3	18.2		38.0	.864
3.23	85.5	16.0		43.2	.982
3.23	85.5	15.8		43.8	.992
3.23	85.5	13.3		52.0	.997
7.10	85.0	10.6		64.9	.996
7.10	85.0	13.1		52.5	.980
7.10	85.0	14.2		48.6	.992
9.82	85.0	14.3		48.4	.962
9.56	85.0	13.3		51.8	.876
9.56	85.3	14.2		48.7	.951
9.56	85.3	13.5		51.2	.990

Comments: The hydrolysis of the ester is a neutral process (same rate at all pH levels). An activation energy of 23,000 cals/mole was used to extrapolate the rate to 25°C.

Water Solubility: 100 ppm

Source: Chemical Services

Listed Purity: None listed. Identity-purity confirmed by spectral analysis.

Analysis Concentration: .46 ppm

Analytical Procedure: Extract 5 ml buffered solution with 2.5 ml isooctane. Dilute 1:1 with internal standard solution (800 ppb TEP in isooctane).

Instrumentation: GC X HPLC ___

Detector: NPD

Columr: DB5 15m, 0.53mm ID

Temperature Program: 100°C Isothermal

5.3.53 O,O,S-Triethylester phosphorodithioic acid

CAS No. 2524-09-6

HYDROLYSIS AND ANALYSIS DATA

Literature Data: A standard for this compound could not be obtained. However the half-life would be less than compound 5.3.52 (the S-ethyl is a better leaving group than O-ethyl).

5.3.54 Tris(2,3-dibromopropy)-phosphate

CAS No. 126-72-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp.°C	$k_1(hr^{-1})$	$k_2(M^{-1}hr^{-1})$	$t_{1/2}$	r^2
3.13	85	0.00177		16.3 d	.671
3.20	85	0.00249		11.6 d	.718
3.20	85	0.00435		6.6 d	.943
7.09	85	0.0923		7.5 hr	.997
7.09	85	0.1004		6.9 hr	.994
7.13	85	0.1125		6.2 hr	.951
8.83	85	2.9507	13855	0.23 hr	.935
8.83	85	3.4572	16234	0.20 hr	.999
9.67	66	2.1379	3492	0.32 hr	.993
9.67	66	2.1258	3472	0.33 hr	.999

Comments: The calculated activation energy and log A for the second-order hydrolysis are 18, 576 ± 1,002 cals/mole and 15.52 ± 0.03 respectively. Hydrolysis at pH 3 was used to calculate the neutral contribution to overall hydrolysis. Hydrolysis of phosphate esters is mediated by the neutral water molecule and hydroxide ion.

Water Solubility: 4 ppm

Source: EPA/RTP or FDA

Listed Purity: 99% Identity-purity confirmed by spectral analysis

Analysis Concentration: 116 ppb

Analytical Procedure: Extract 10 ml buffer containing tris with 2 ml isooctane. Add 3 ml isooctane and inject 1 ml onto GC.

Extraction Solvent: Isooctane

Instrumentation: GC X HPLC ___

Detector: EC

Column: 10m, SE-54 thin film (approximately 0.1 micron)

Temperature Program: 205°C for 0.5 min then 8°C/min to 230°C.

5.3.54 Tris (2,3-Dibromopropyl) phosphate

$K_1 = 2.1\ hr^{-1}$

$T_{1/2} = 0.3\ hr$

$R^2 = 0.993$

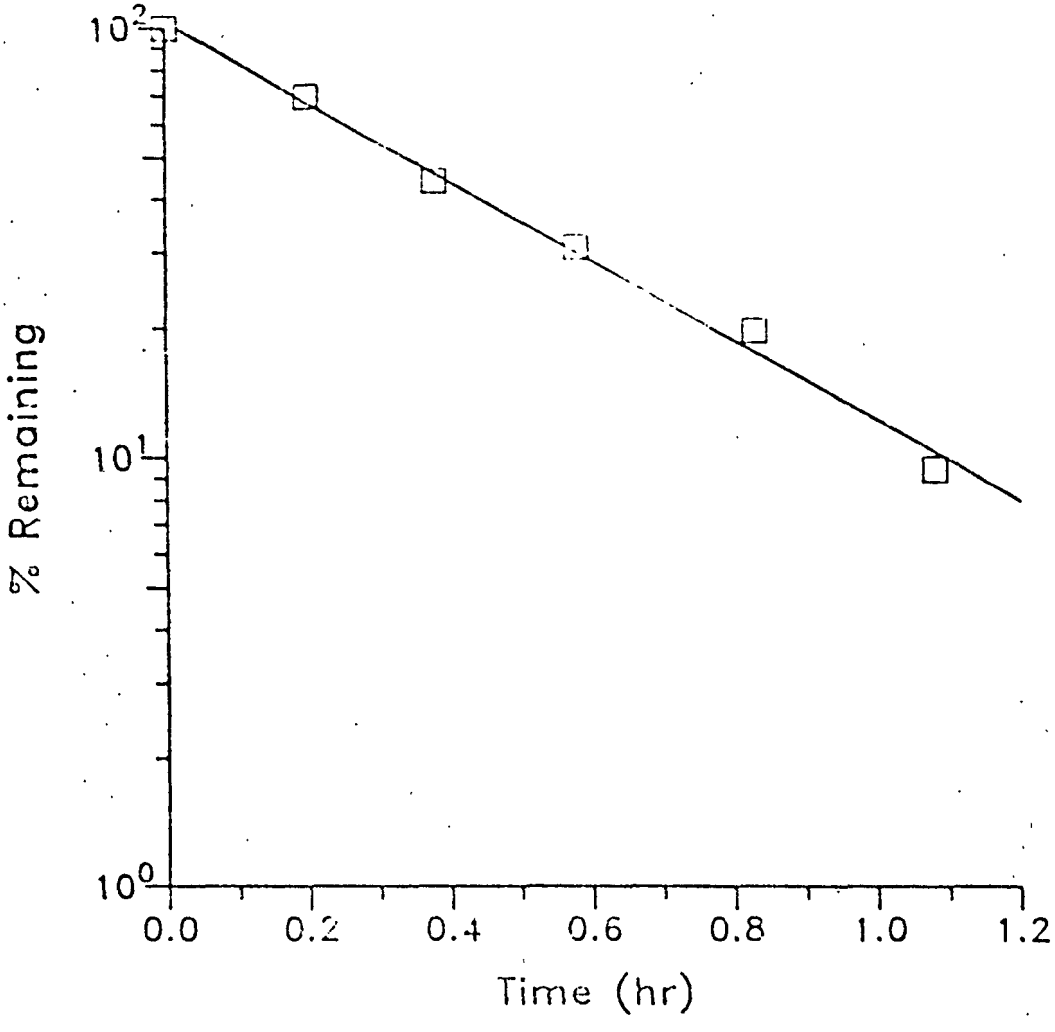

Figure 5.3.54 Hydrolysis of Tris (2,3-Dibromopropyl) phosphate at 66°C, pH 9.6

APPENDIX A

MASS SPECTROMETRIC ANALYSIS

Objective: The objective of this MS work was to check the identity of the following chemicals: N-(aminothioxomethyl)acetamide, 1-(o-chlorophenyl)thiourea, 3-chloropropanenitrile, O,O-diethyl-Opyrazinyl phosphorothioate, 2,4-dithiobiuret, 2-fluoroacetamide, isodrin, alpha-napthylthiourea, octamethylpyrophosphoramide, toxaphene, acetonitrile, 2-acetylaminofluorene, cis-chlordane, trans-chlordane, 1,2-dichloropropane, diallate, p,p'-DDD, di-n-octylphthalate, hexachlorobenzene, lindane, hexachloroethane, lasiocarpine, malononitrile, methylthiouracil, thioacetamide, thiram, methyl methacrylate, azaserine, chlorambucil, heptachlor, and kepone. These chemicals are used as standards for determining the "second-third" hydrolysis rate constants. The mass spectrum of each standard was determined by either GC/MS or probe/MS.

Apparatus and conditions: Analyses were carried out with a Finnigan Model 4500 gas chromatograph - mass spectrometer interfaced to the Finnigan Incos Data System. The mass spectral matching program used the "1984 EPA/NIH Incos Compatible Library Containing 42,197 Mass Spectra" obtained from W. L. Budde of EMSL-Cinn (EPA/NIH Library). The 1983 version of the bound "EPA/NIH Mass Spectral Database" and the 1983 version of the "Eight Peak Index of Mass Spectra" were also used as references.

The GC column was a DB-5 fused capillary 30m X 0.25mm; for most chemicals, the temperature program was 3 min at 45°C, 45-280°C at 10°/min. Acetonitrile, because of its volatility, was injected directly on the column at room temperature. Lasiocarpine, azaserine, thiram, N-(aminothioxomethyl)acetamide, 1-(O-chlorophenyl)-thiourea, 2,4-dithiobiuret, and 2-fluoroacetamide could not be analyzed by GC; they were analyzed from a direct probe at 75-200°C.

RESULTS

Standard Reference Compounds

N-(Aminothioxomethyl)acetamide: The probe mass spectrum was an excellent match to the standard spectrum of N-(aminothioxomethyl)acetamide in the EPA/NIH Library.

1-(o-Chlorophenyl)thiourea: The probe mass spectrum was not in any available database. The fragmentation pattern, however, shows characteristics expected for 1-(O-chlorophenyl)thiourea. There is a prominent molecular ion at m/z 186 with a chlorine isomer pattern indicating one chlorine. The base peak at m/z 151 represents a chlorine loss; the ion at m/z 127 represents a chlorophenyl-NH_2 group.

3-Chloropropanenitrile: The GC mass spectrum was an excellent match to the standard spectrum of 3-chloropropanenitrile in the EPA/NIH Library.

0,0-Diethyl-0-pyrazinyl phosphorothioate: The GC mass spectrum was an excellent match to the standard spectrum of 0,0-diethyl-0-pyrazinyl phosphorothioate ir the EPA/NIH Library.

2,4-Dithiobiuret: The probe mass spectrum was not in any available database. The fragmentation pattern shows characteristics expected of 2,4-dithiobiuret. There is a prominent molecular ion at m/z 135 with an 8.8% m/z 137 ion indicating 2 sulfur groups. A large m/z 60 ion represents a $-CSNH_2$ group.

2-Fluoroacetamide: The probe mass spectrum was not in any available database. The fragmentation pattern, however, shows characteristics expected of 2-fluoroactamide. There is a prominent molecular ion at m/z 77. The m/z 60 ion represents a loss of -OH.

Isodrin: The GC mass spectrum was an excellent match to the standard spectrum of isodrin in the EPA/NIH Library.

alpha-Naphthylthiourea: The compound decomposes on a GC column to 2-isothiocyanato naphthalene. There is an excellent match to the standard spectrum of 2-isothiocyanato naphthalene in the EPA/NIH Library.

Octamethylpyrophosphoramide: The GC mass spectrum was an excellent match to the standard spectrum of octamethylpyrophosphoramide in the EPA/NIH Library.

Toxaphene: Toxaphene is a mixture of many compounds produced by the chlorination of camphene. Toxaphene gives a characteristic smear when analyzed by GC and is best identified by this profile. The mass spectra is not revealing, only showing a highly chlorinated family of compounds. The GC-MS ion chromatogram of this toxaphene standard matches the toxaphene profile in "Analysis and GC-MS Characterization of Toxaphene in Fish and Water" by David L. Stallings, EPA-600/3-76-076, August, 1976.

Acetonitrile: The GC mass spectrum was an excellent match to the standard spectrum of acetonitrile in the EPA/NIH Library.

2-Acetylaminofluorene: The GC mass spectrum was an excellent match to the standard spectrum of 2-acetylaminofluorene in the EPA/NIH Library.

cis-Chlordane: The GC mass spectrum was a good match to the standard spectrum of chlordane in the EPA/NIH Library. The mass spectra of the cis and trans isomers of chlordane are very similar and cannot be distinguished from each other. The GC retention times of the two compounds are quite different, however.

trans-chlordane: The GC mass spectrum was a good match to the standard spectrum of chlordane in the EPA/NIH Library. The mass spectra of the cis and trans isomers of chlordane are very similar and cannot be distinguished from each other.

1,2-Dichloropropane: The GC mass spectrum was a good match to the standard spectrum of 1,2-dichloropropane in the EPA/NIH Library.

Diallate: The gas chromatograph separates diallate's cis and trans isomers into two separate peaks. The GC mass spectrum of each was a good match to the standard spectrum of diallate in the EPA/NIH Library. The mass spectra of the two isomers are very similar and cannot be distinguished from each other.

p,p'-DDD: The GC mass spectrum was a good match to the standard spectrum of p,p'-DDD in the EPA/NIH Library.

Di-n-Octylphthalate: The GC mass spectrum was a good match to the standard spectrum of di-n-octylphthalate in the EPA/NIH Library.

Hexachlorobenzene: The GC mass spectrum was an excellent match to the standard spectrum of hexachlorobenzene in the EPA/NIH Library.

Lindane: The GC mass spectrum was a good match to the standard spectrum of lindane in the EPA/NIH Library.

Hexachloroethane: The GC mass spectrum was an excellent match to the standard spectrum of hexachloroethane in the EPA/NIH Library.

Lasiocarpine: The probe mass spectrum was a good match to the standard spectrum of lasiocarpine in the EPA/NIH Library.

Malononitrile: The GC mass spectrum was a good match to the standard spectrum of malononitrile in the EPA/NIH Library.

Methylthiouracil: The GC mass spectrum was not in any available database. The fragmentation pattern, however, shows characterstics expected for methylthiouracil. There is a prominent molecular ion at m/z 142. There is a large m/z 68 ion representing a loss of -HNCSNH.

Thioacetamide: The GC mass spectrum was a good match to the standard spectrum of thioacetamide in the EPA/NIH Library.

Thiram: The probe mass spectrum was a good match to the standard spectrum of thiram in the EPA/NIH Library.

Methyl Methacrylate: The GC mass spectrum was a good match to the standard spectrum of methyl methacrylate in the EPA/NIH Library.

Azaserine: The probe mass spectrum was not in any available database. The fragmentation pattern, however, shows characteristics expected for azaserine. The highly reactive NN group apparently protonates giving a protonated molecular ion at m/z 174. There is a characteristic acid loss -COOH (plus a protonated ion) at m/z 128; ions at m/z 69, and 74 represents -COCHNN and $-HCNH_2COOH$, respectively.

Chlorambucil: The probe mass spectrum was not in any available database. The fragmentation pattern, however, shows characteristics expected for chlorambucil. There is a prominent molecular ion at m/z 303, with a chlorine isomer pattern indicating two chlorines. The base peak at m/z 254, represents a $-CH_2Cl$ loss.

Heptachlor: The GC mass spectrum was a good match to the standard spectrum of heptachlor in the EPA/NIH Library.

Kepone: The GC mass spectrum was a good match to the standard spectrum of Kepone in the EPA/NIH Library.

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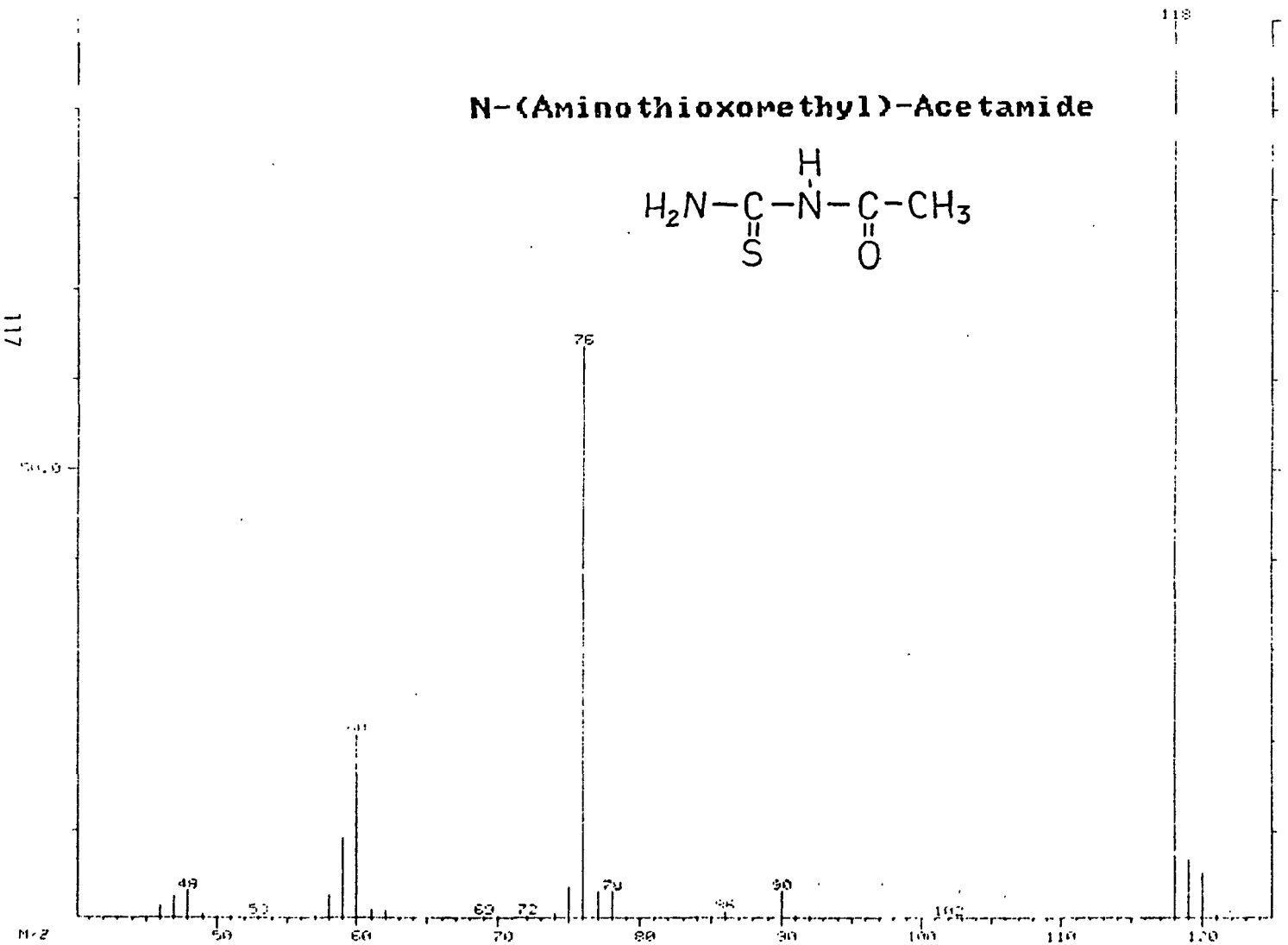
CHLI: C317 #2



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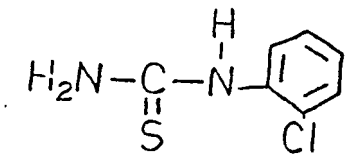
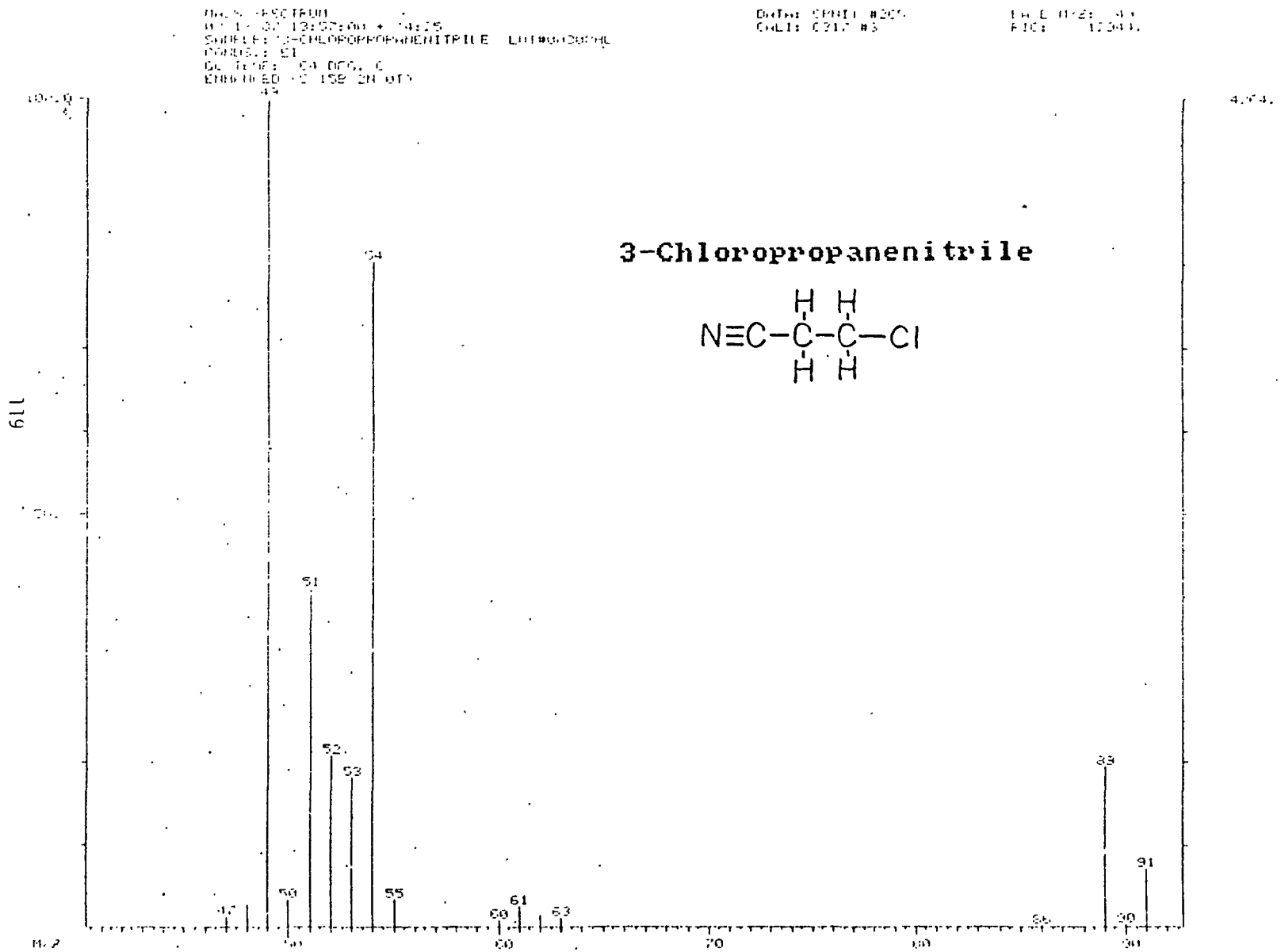
SAMPLE: 1-(2-CHLOROPHENYL)-2-THIOUREA UNIT#GP03311JR
COMMENT: EI-PROBE

ON-THE OFFICE #12
CHEM: FILE #2

1-(o-Chlorophenyl)thiourea

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N≡C–C(H)(H)–C(H)(H)–Cl
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54
51
52
53
50
55
60
61
63
39
91
90
119

MASS SPECTRUM
02/05/87 15:13:00 + 0:52
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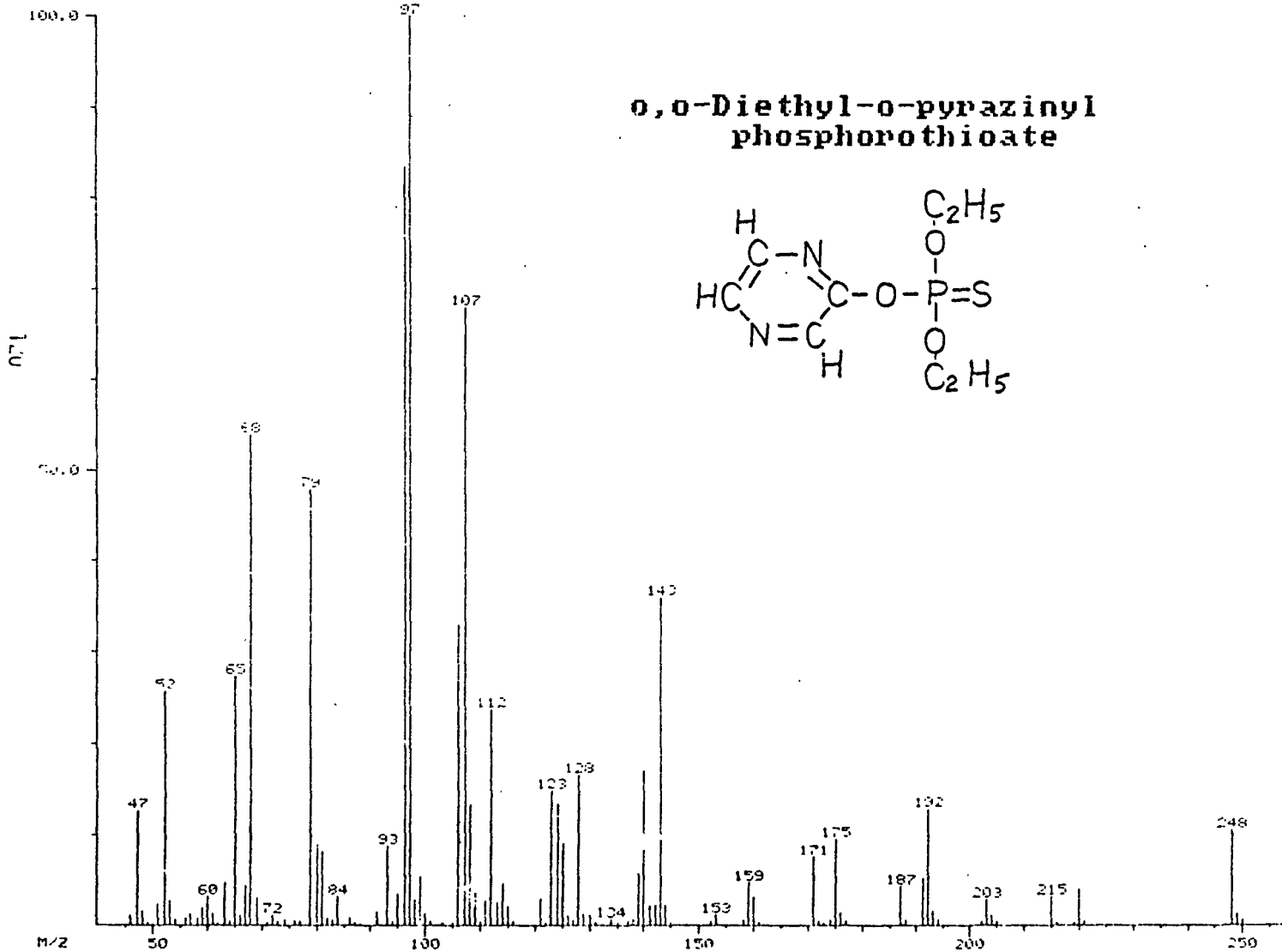
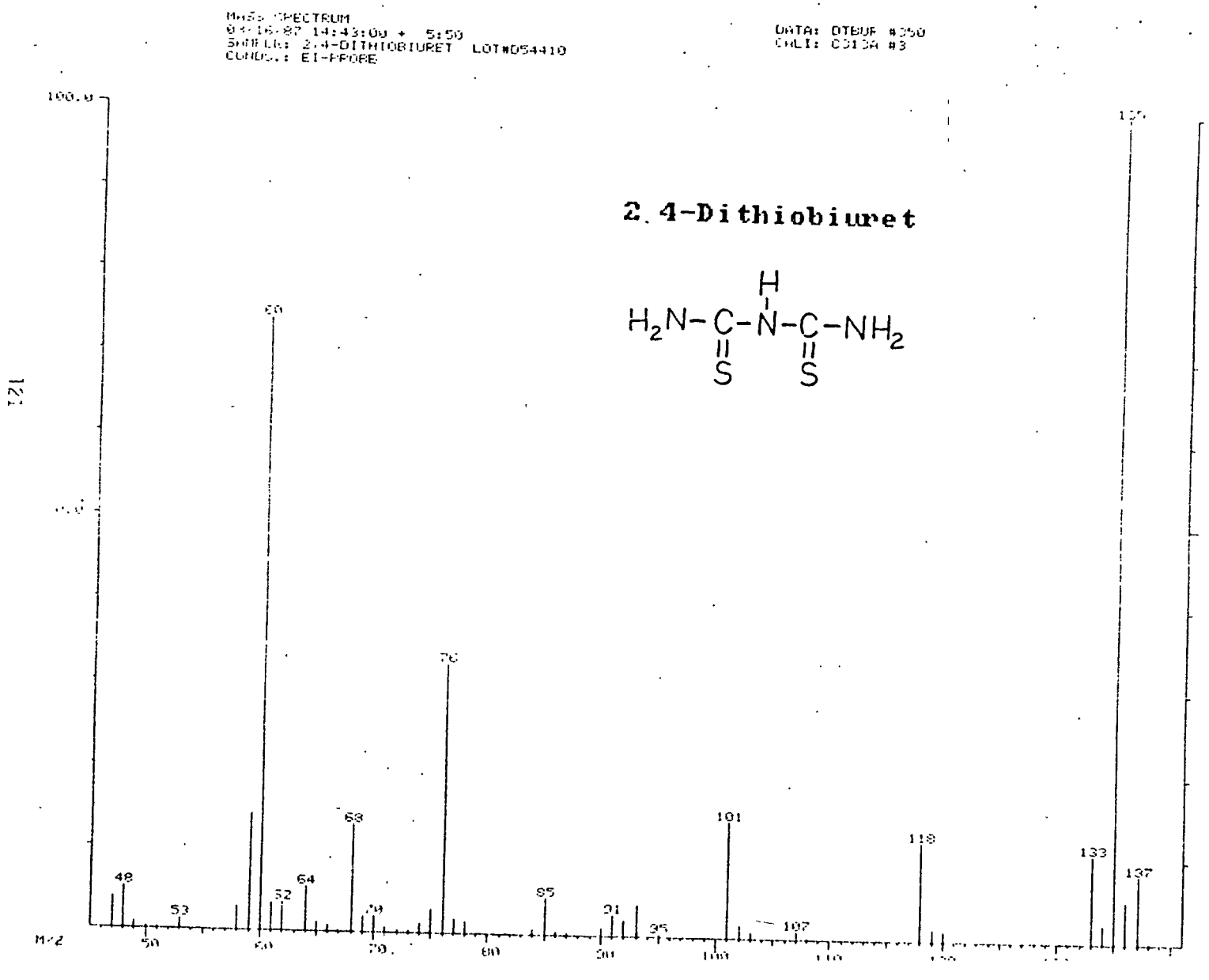
COND.: EI

DATA: DPP #52
CALI: CFEB87 #3

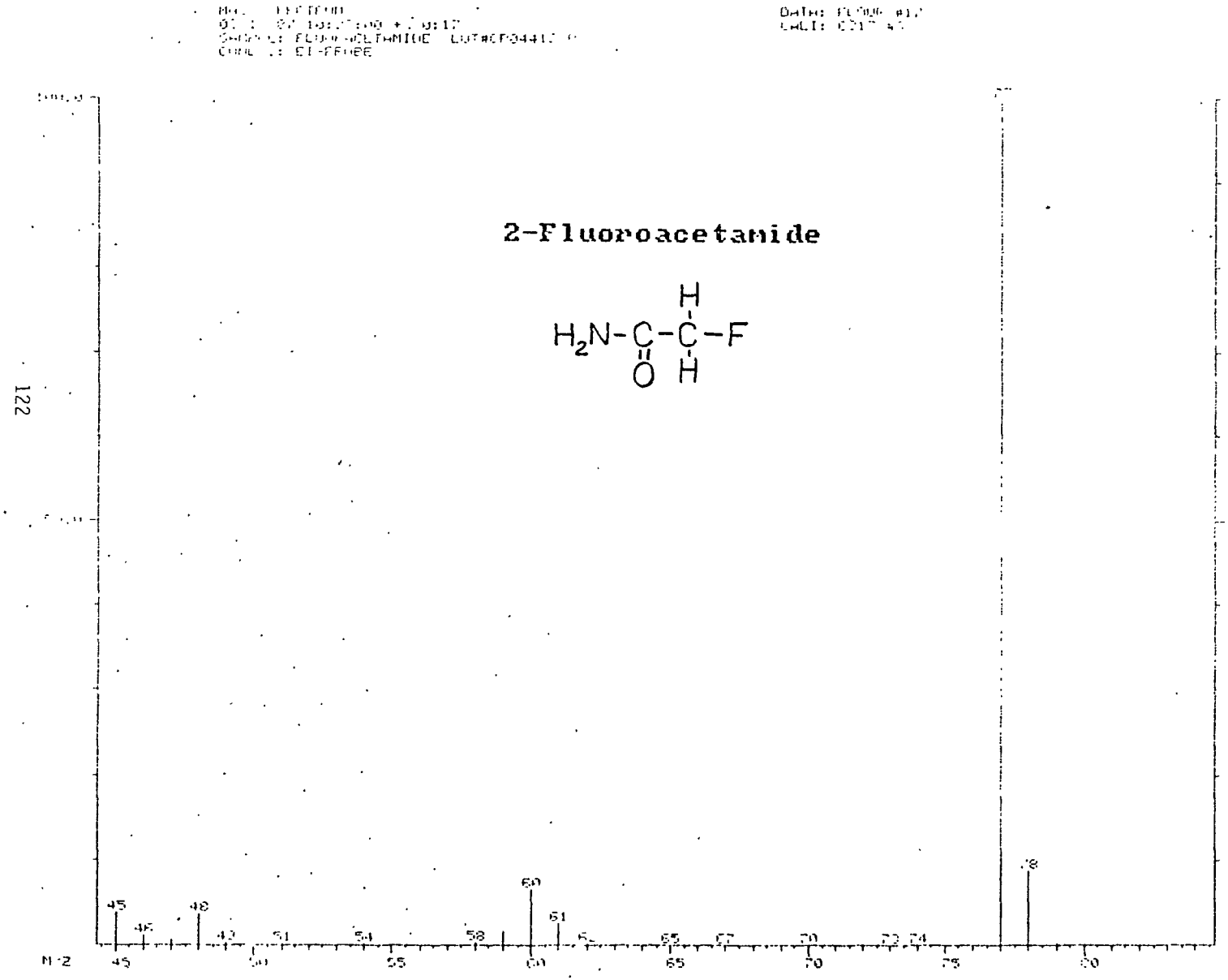


O,O-Diethyl-O-pyrazinyl phosphorothioate



2,4-Dithiobiuret

$$H_2N-\overset{\overset{S}{\|}}{C}-\overset{\overset{H}{|}}{N}-\overset{\overset{S}{\|}}{C}-NH_2$$


2-Fluoroacetanide
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M/Z
45
48
60
61
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50
55
60
65
70
75
80

MASS SPECTRUM
02/04 87 3:57:00 + 21:32
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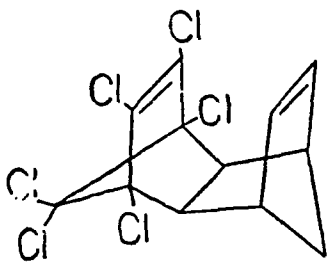
CONDS.: EI
GC TEMP: 233 DEG. C

DATA: ISODR #1232
CALI: CFEB3 #1

Isodrin



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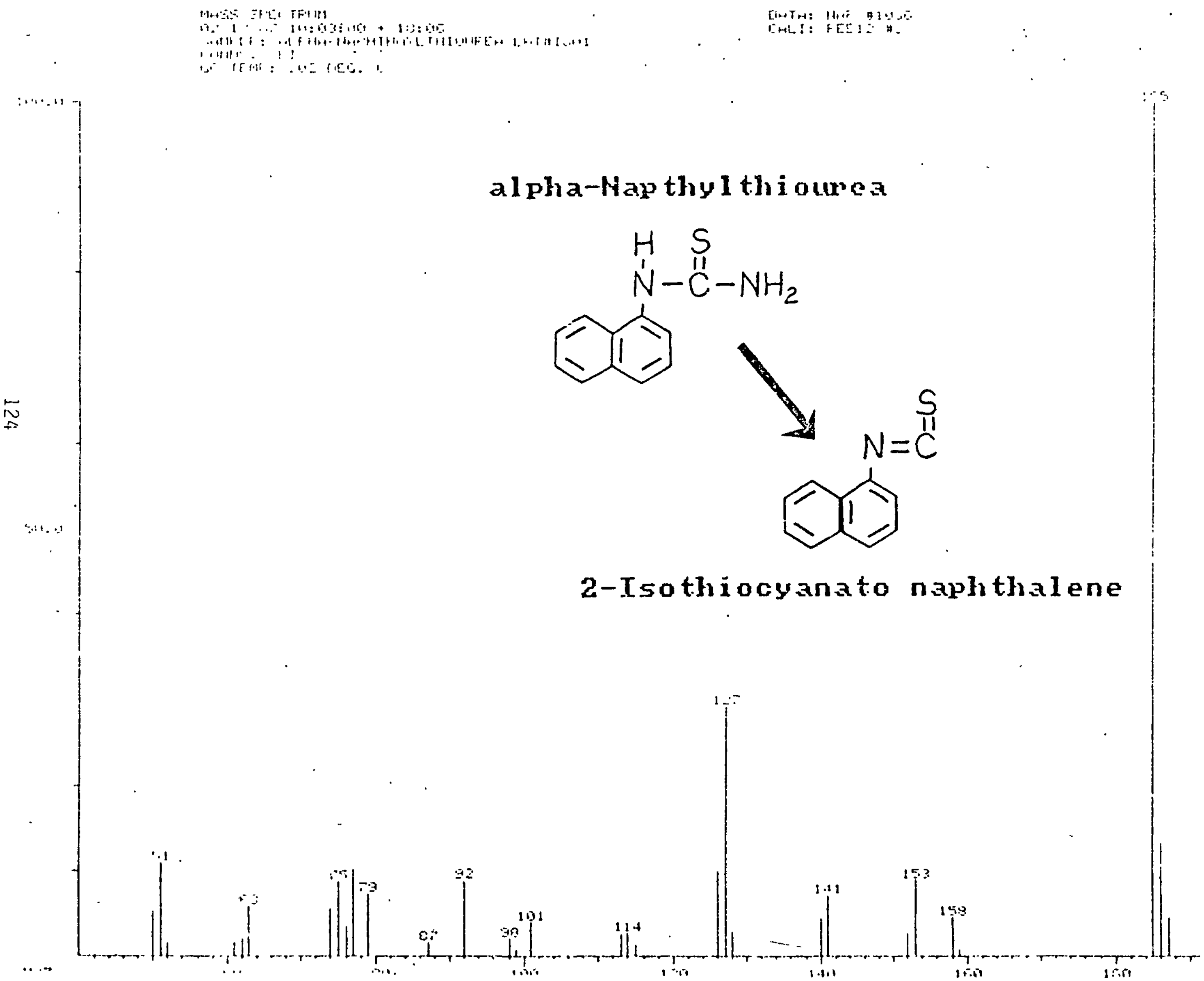
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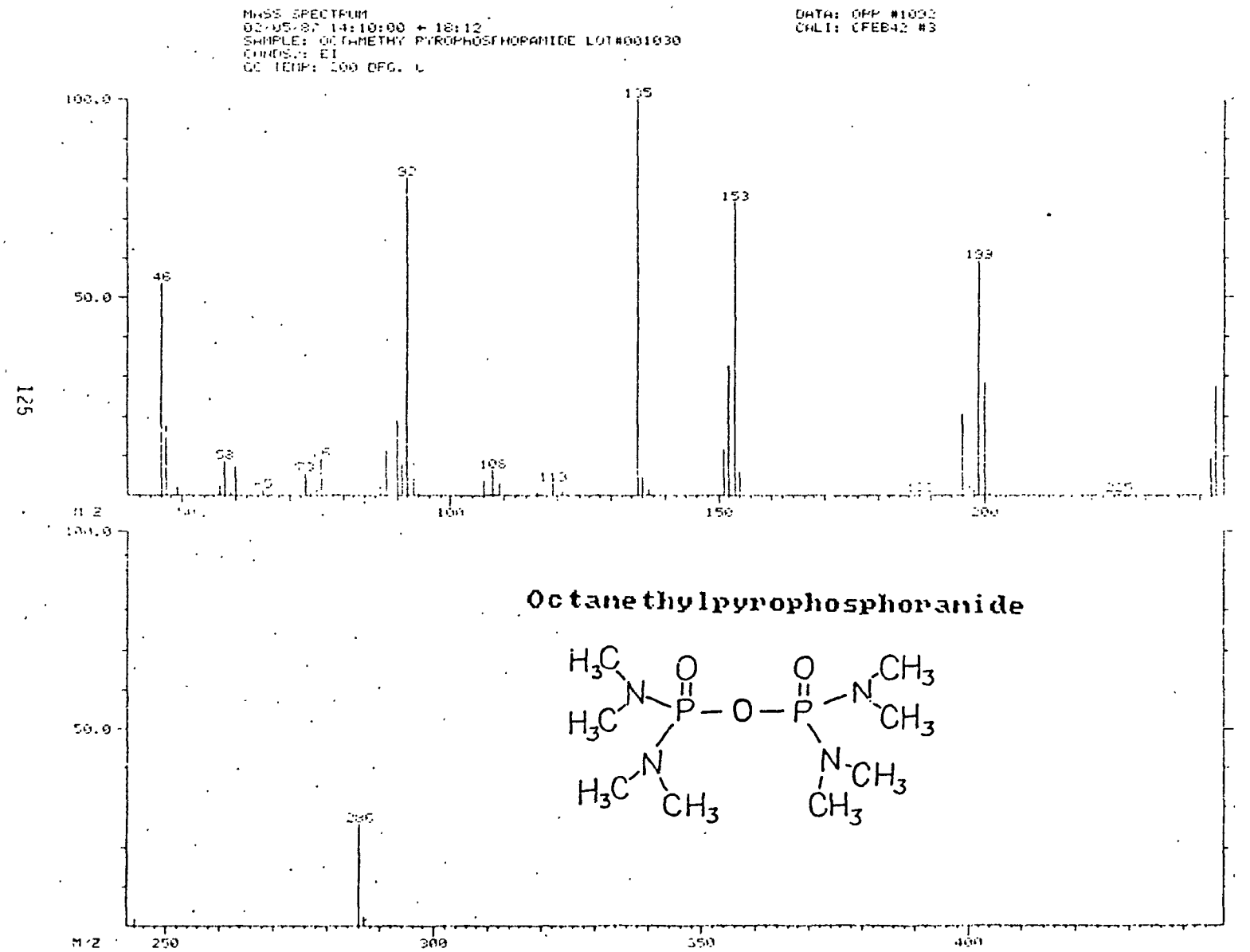
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CALI: CFEB42 #3
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50.0
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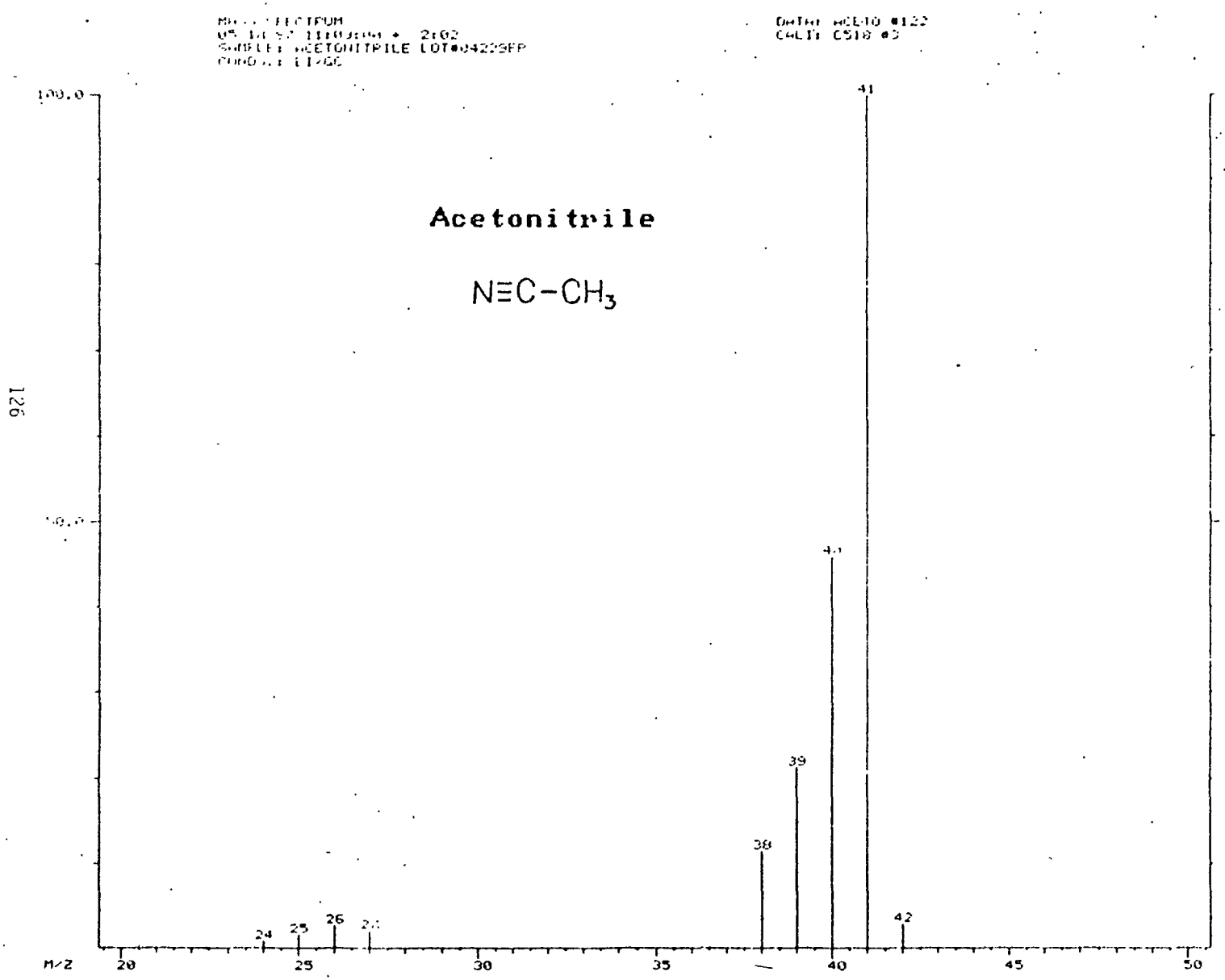
Octanethylpyrophosphoramide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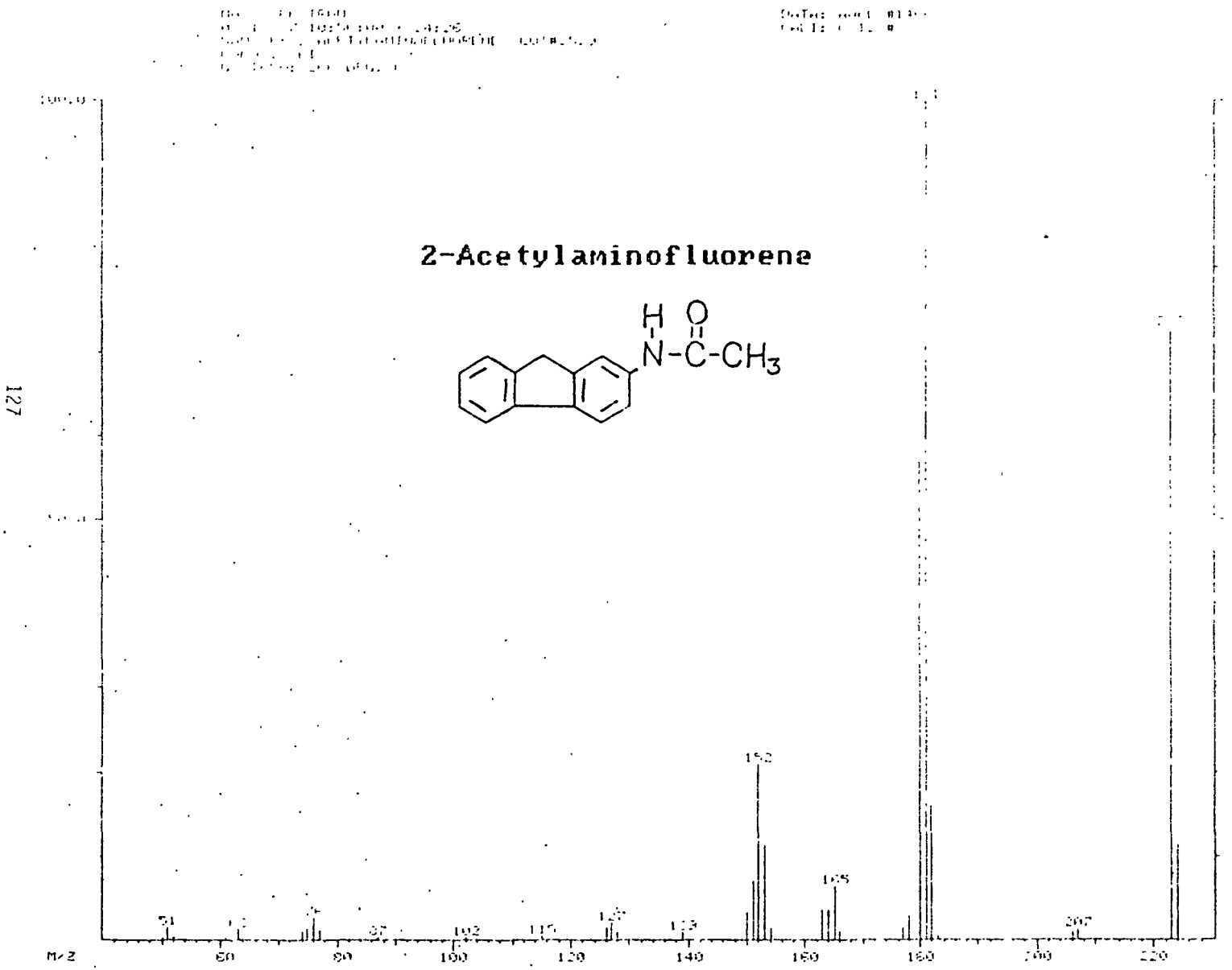
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M/Z
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51
65
89
102
115
152
165
207

MASS SPECTRUM
07-JUN-87 10:45:00 + 22:32
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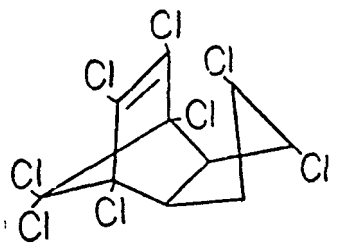
CONDS.: E1
GC TEMP: 240 DEG. C

DATA: NCHLOP #1552
CAL.: CFEB3 #3

cis-Chlordane



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SAMPLE: GAMMA CHLORDANE LOT#F505 STD
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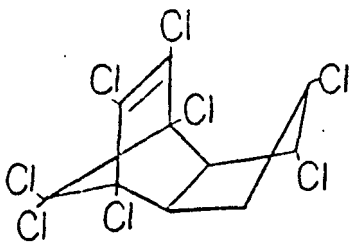
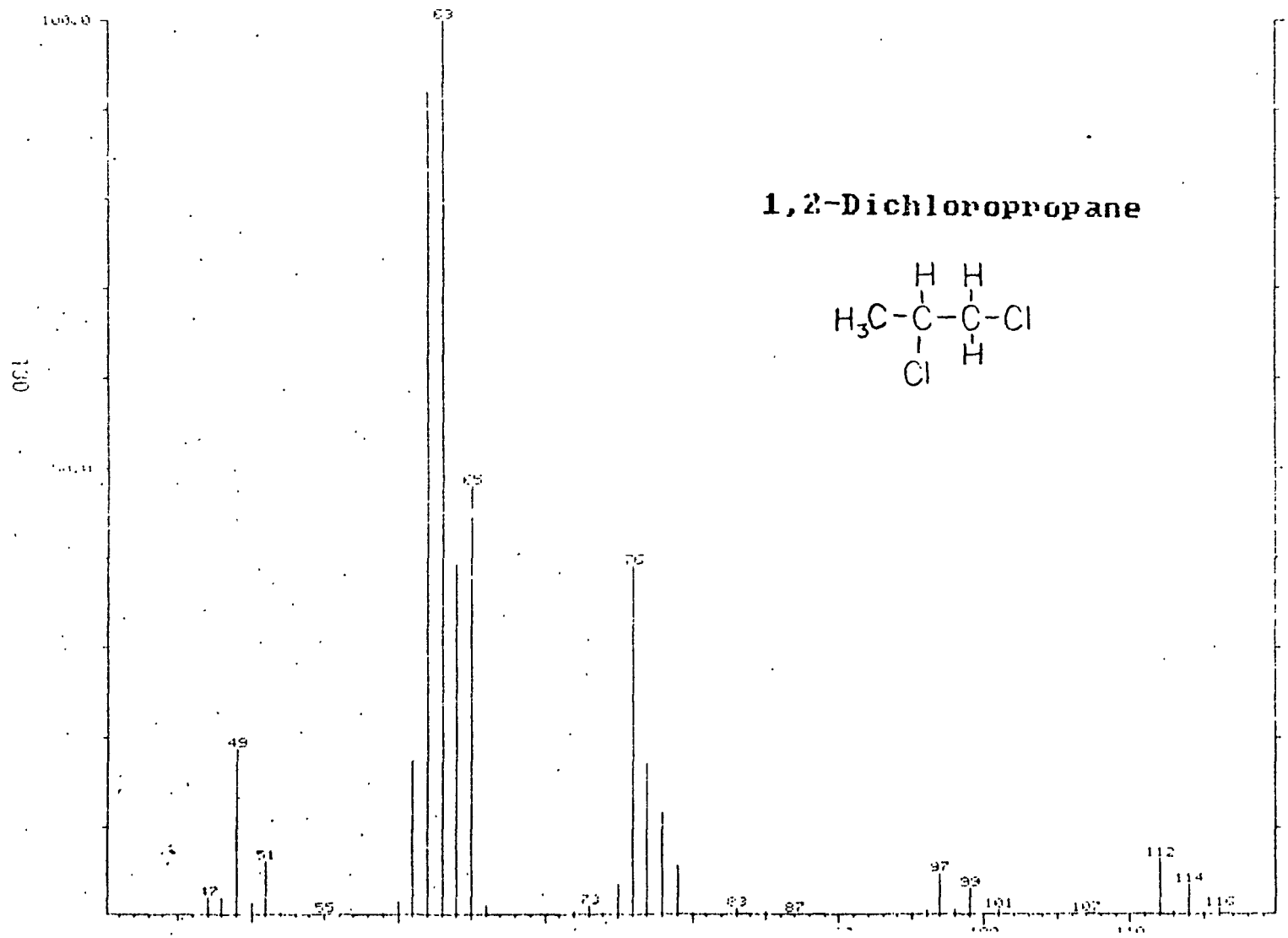
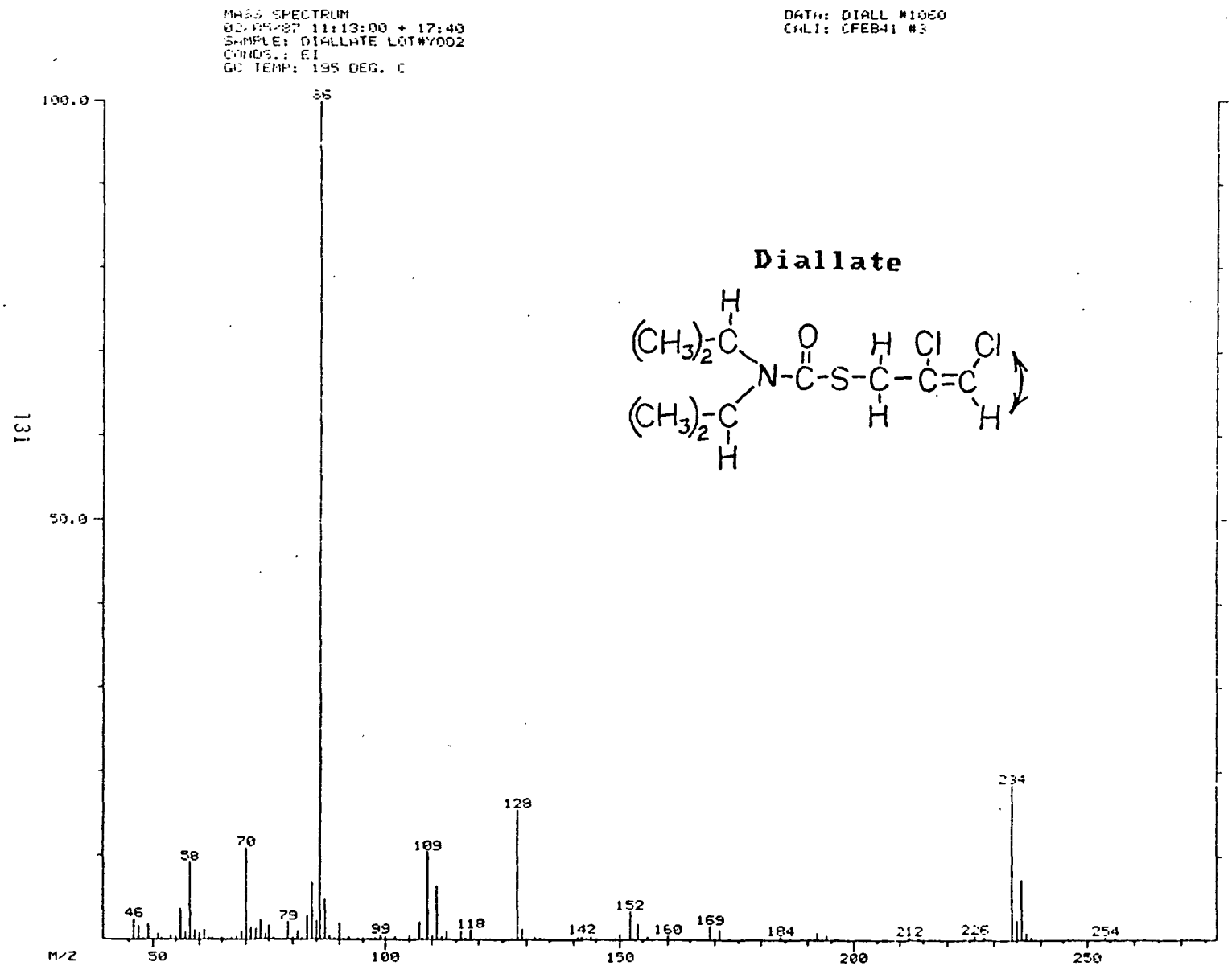
GC TEMP: 250 DEG. C

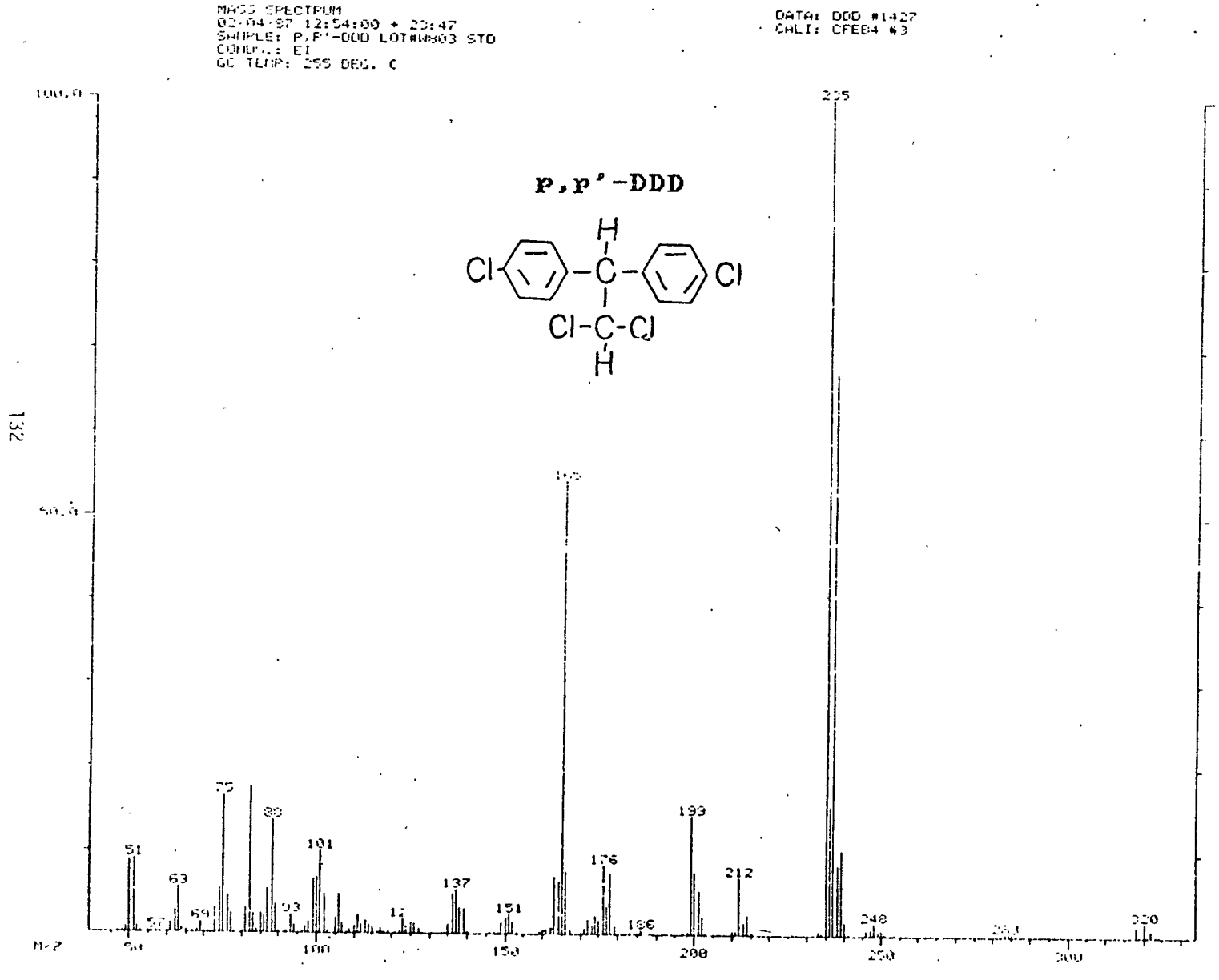
DATA: GCNLOR #1333
CALI: CFED4 #3

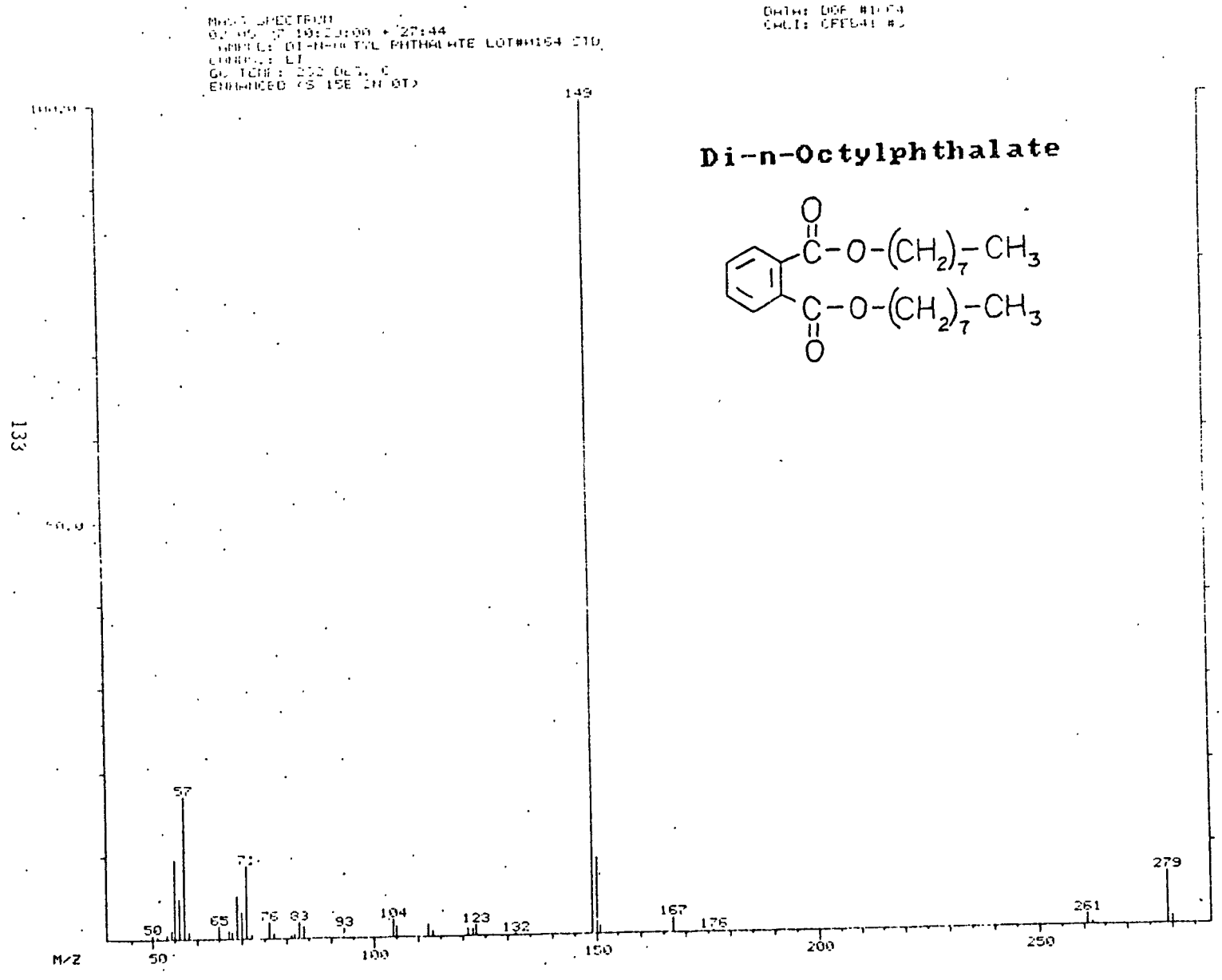
trans-Chlordane




1,2-Dichloropropane
63
65
76
49
51
97
112
114
130


MASS SPECTRUM
02/09/87 11:13:00 + 17:40
SAMPLE: DIALLATE LOT#YD02
CONDS.: EI
GC TEMP: 195 DEG. C
DATA: DIALL #1060
CALI: CFEB41 #3
Diallate
100.0
50.0
131
M/Z
50
100
150
200
250
86
58
70
109
128
234
46
79
99
118
142
152
160
169
184
212
226
254

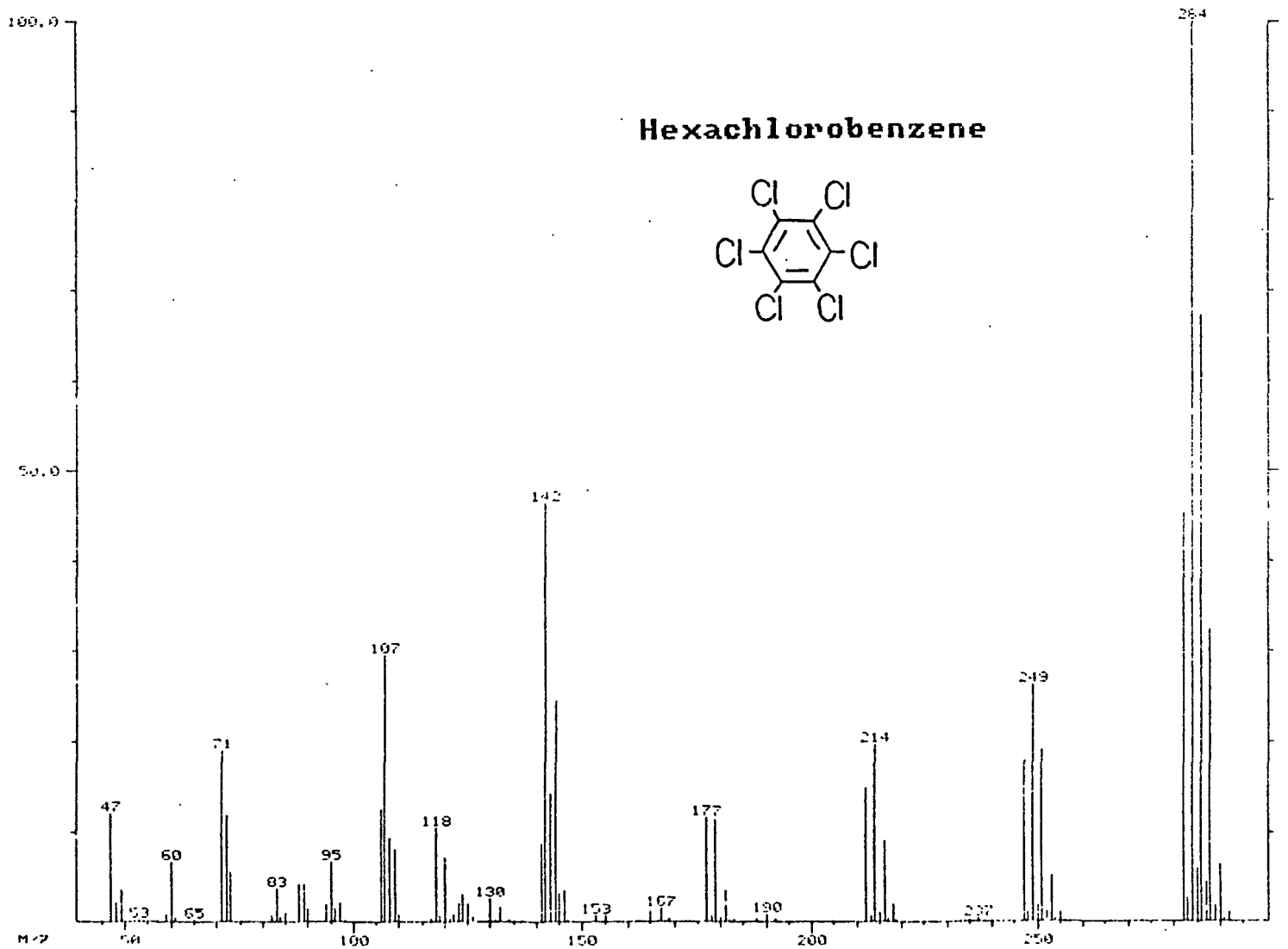

MASS SPECTRUM
02-04-87 12:54:00 + 20:47
SAMPLE: P,P'-DDD LOT#W803 STD
COND.: EI
GC TEMP: 255 DEG. C
DATA: DDD #1427
CALI: CFEB4 #3
p,p'-DDD
Cl
Cl
Cl-C-Cl
H
H
132
100.0
50.0
M/Z
50
100
150
200
250
300
51
63
75
88
101
137
151
176
193
212
235
248
320



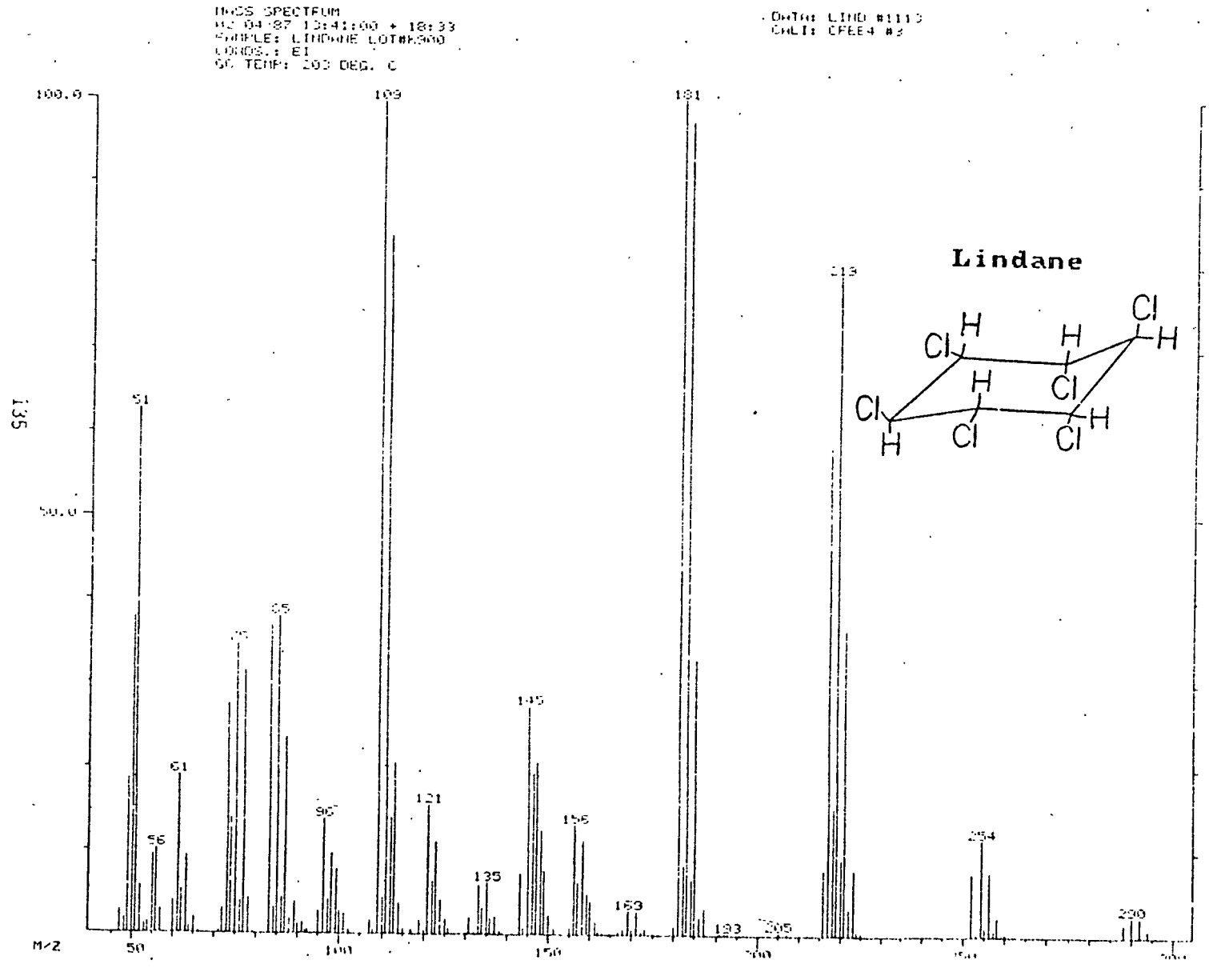
Di-n-Octylphthalate

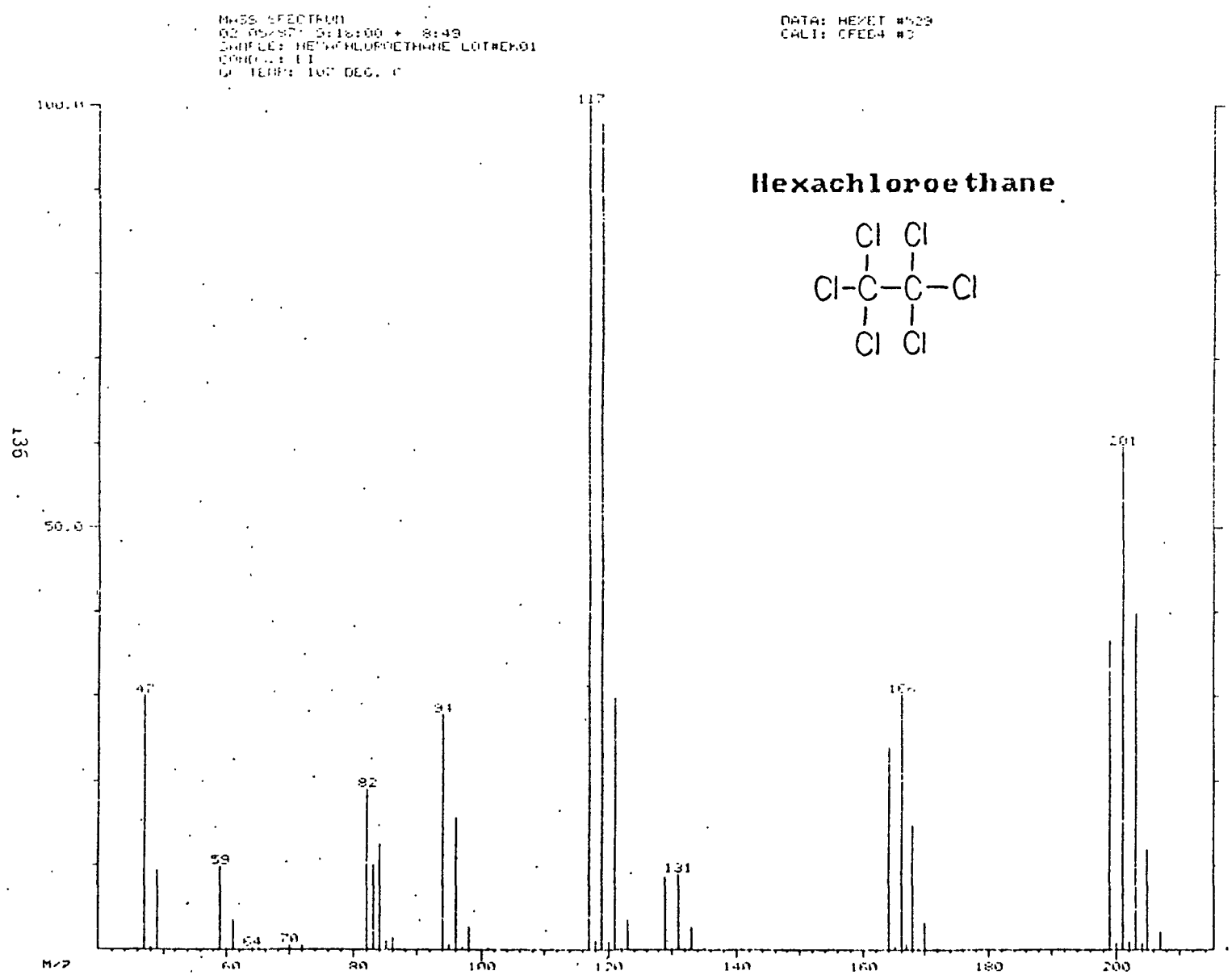
MASS SPECTRUM
02/04/97 14:17:00 + 17:58
SAMPLE: HEXACHLOROBENZENE LOT#E04L
CONDS.: EI
GC TEMP: 197 DEG. C

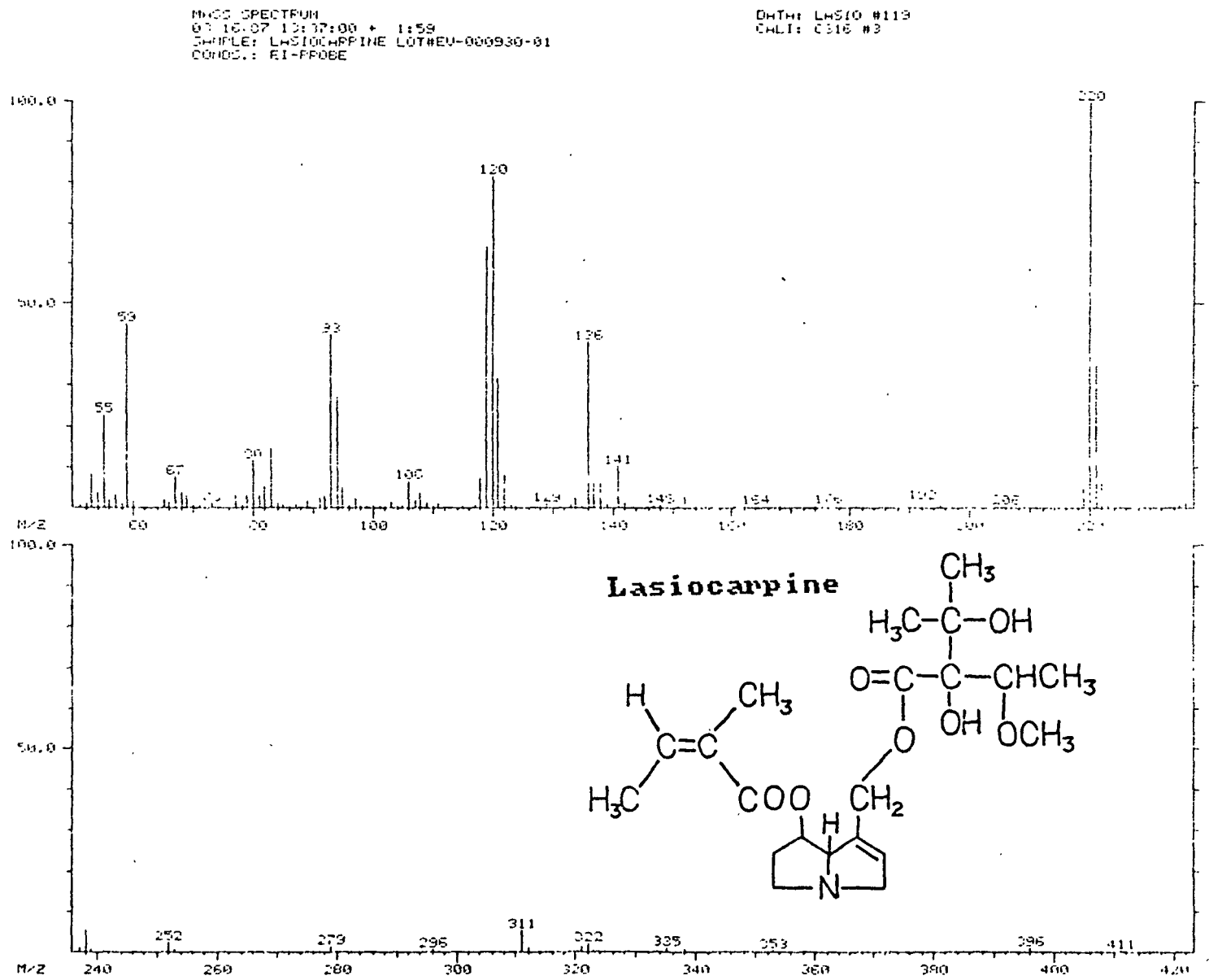
DATA: HEXCB #1078
CALI: CFEB4 #3



Hexachlorobenzene


INCOS SPECTRUM
SAMPLE: LINDANE LOT#K900
IONIS.: EI
SC TEMP: 200 DEG. C
DATA: LIND #1113
CHLI: CPEE4 #2
Lindane
100.0
50.0
135
M/Z
109
181
213
254
51
61
65
75
96
121
135
145
155
163
193
205
290
Cl
H

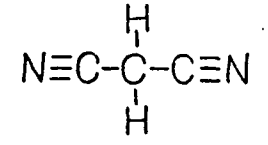

MASS SPECTRUM
02 05/87 9:10:00 + 8:49
SAMPLE: METHACHLOROETHANE LOT#EK01
CONDI: EI
SP TEMP: 107 DEG. C
DATA: HEXET #529
CALI: CFEB4 #3
Hexachloroethane
Cl Cl
Cl-C-C-Cl
Cl Cl
100.0
50.0
%
M/Z
47
59
64
70
82
91
117
131
166
201
60
80
100
120
140
160
180
200


MASS SPECTRUM
01 16:07 13:37:00 + 1:59
SAMPLE: LASIOCARPINE LOT#EV-000930-01
CONDS.: EI-PROBE
DATA: LASIO #113
CALI: C316 #3
100.0
50.0
M/Z
55
69
67
83
97
106
120
136
141
220
60
80
100
120
140
160
180
200
240
260
280
300
320
340
360
380
400
420
252
279
296
311
322
335
353
396
411
Lasiocarpine
CH3
H3C-C-OH
O=C-C-CHCH3
OH OCH3
O
CH2
H
N
H
CH3
C=C
H3C
COO

MASS SPECTRUM
[illegible] 98:15:00 + 5:07
SAMPLE: MALONONITRILE LOT#00126HH
COND.: EI
SO. TEMP: 70 DEG. C

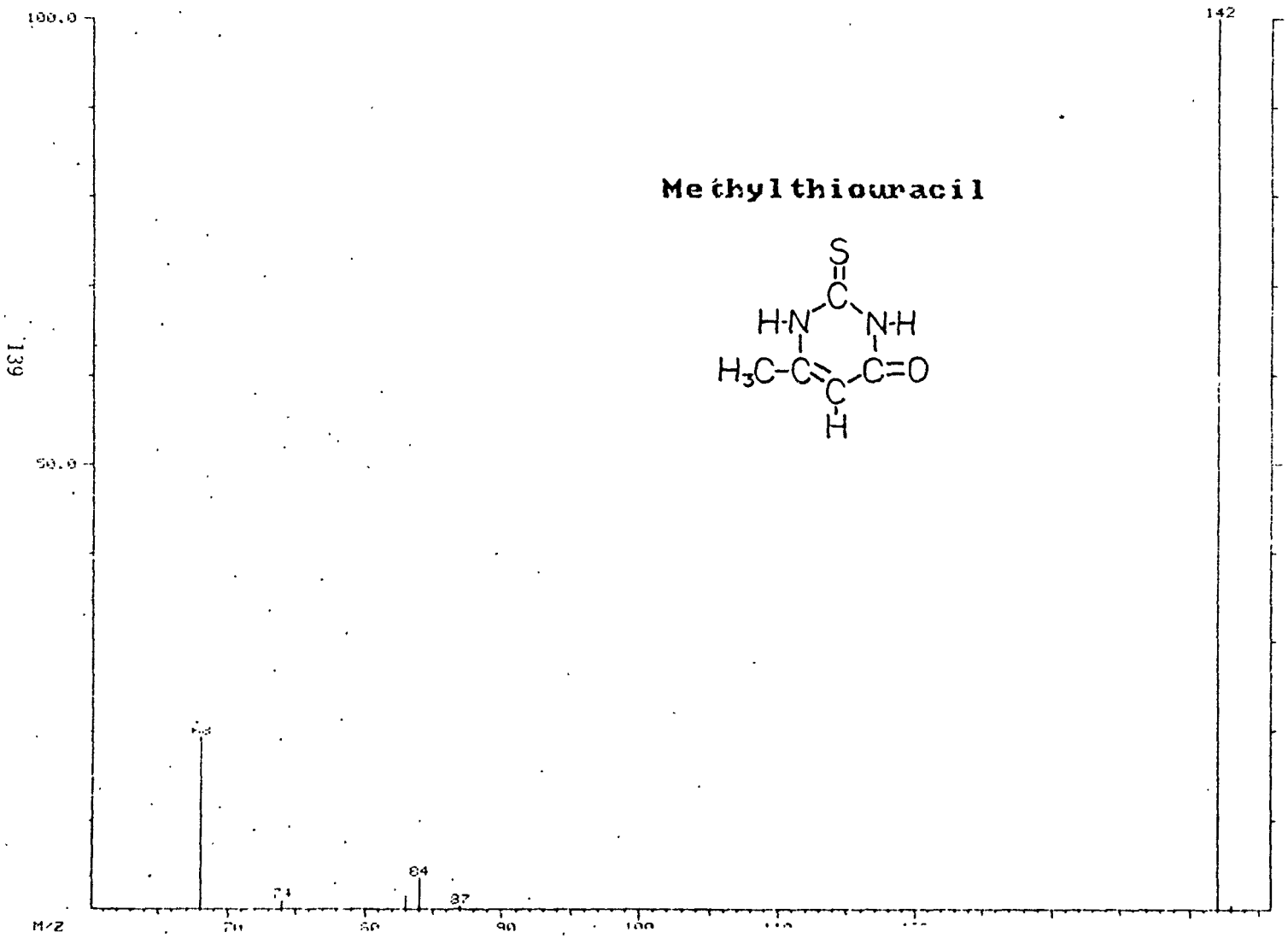
SMITH: DMLO #[illegible]
CMLI: C313 #[illegible]

Malononitrile

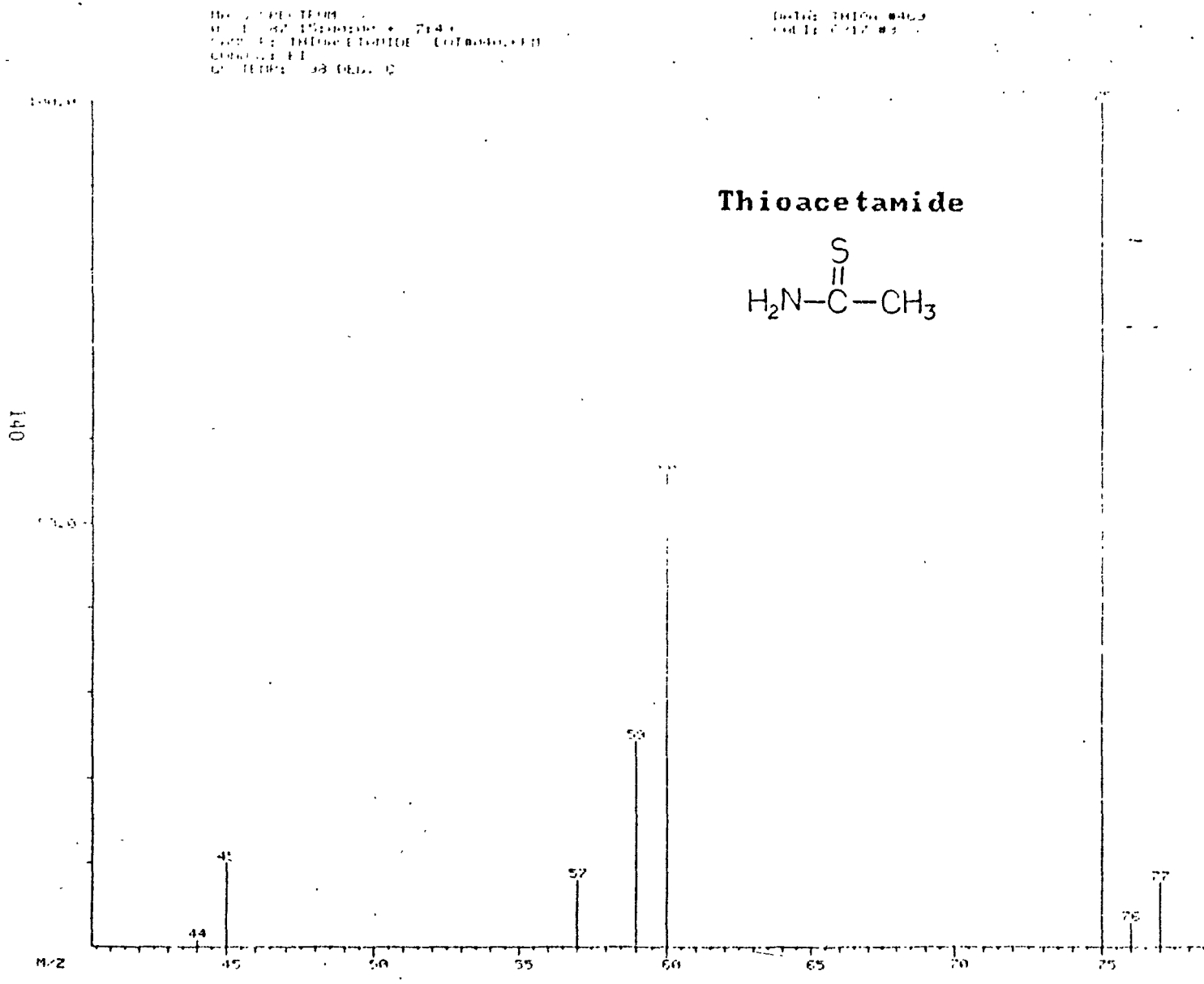


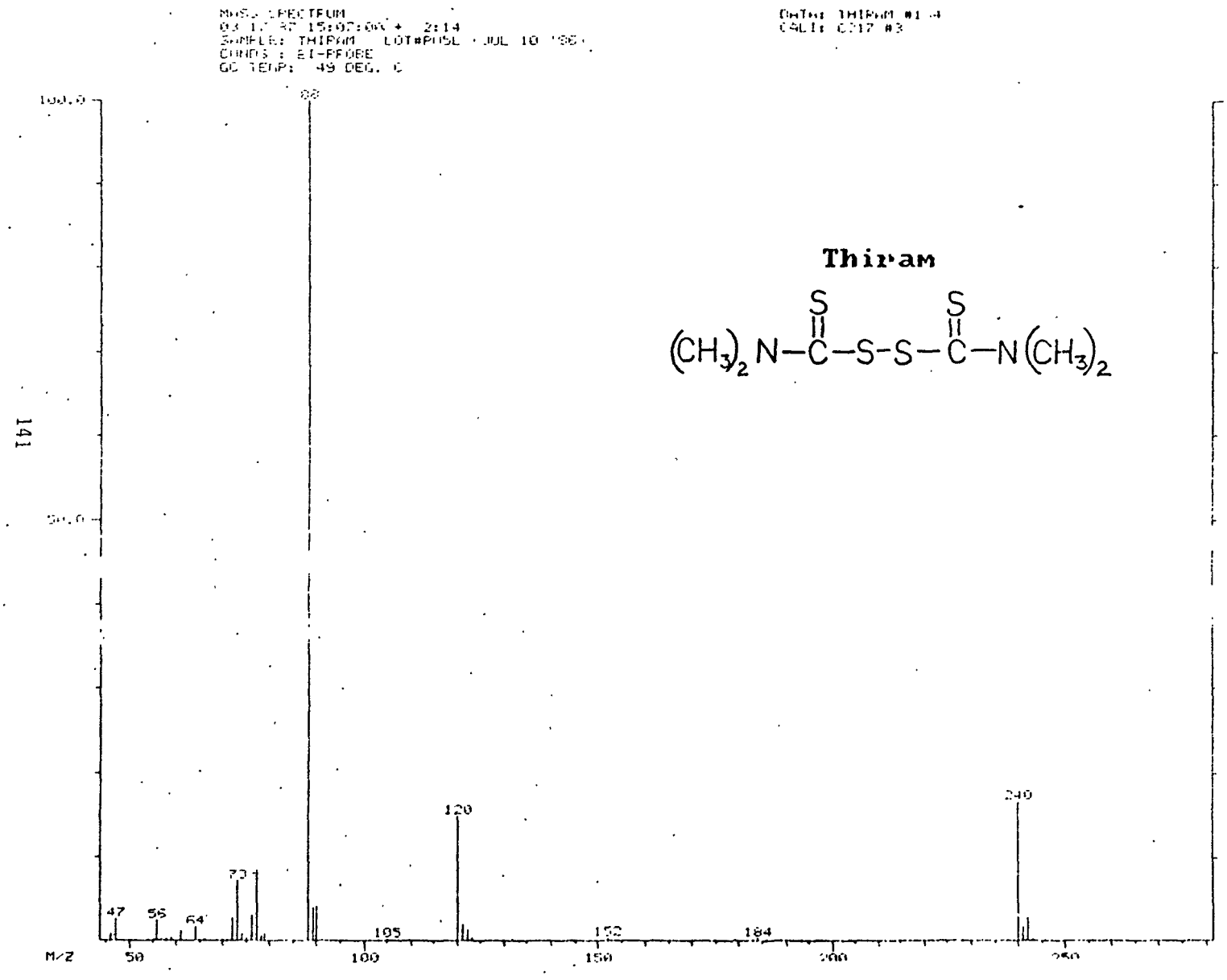
MASS SPECTRUM
07 13:87 10:41.00 + 19:13
SAMPLE: METHYLTHIOURACIL LOT#MM1 0412PTK
CONDS.:
GC TEMP: 214 DEG. C

DATA: METHU #1159
CALI: CS13 #3



Methylthiouracil


Thioacetamide
S
H2N–C–CH3
140
M/Z
44
45
57
59
75
76
77
45
50
55
60
65
70
75

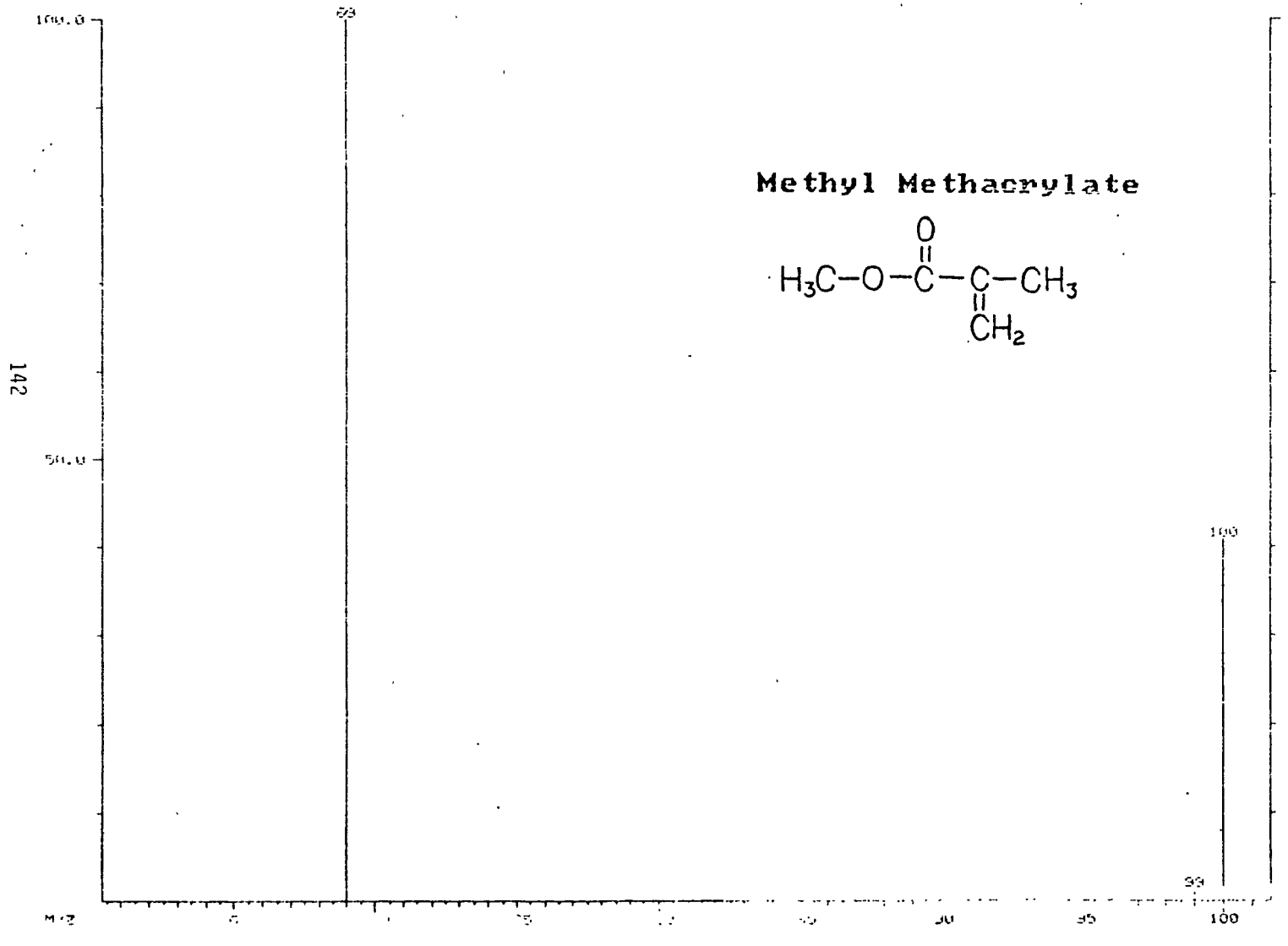

MASS SPECTRUM
SAMPLE: THIRAM LOT#P105L - JUL 10 '86
CONDS : EI-PROBE
GC TEMP: 49 DEG. C
DATA: THIRAM #1-4
CALI: C17 #3
100.0
50.0
141
M/Z
47
56
64
73
120
195
152
184
240
50
100
150
200
250

Thiram

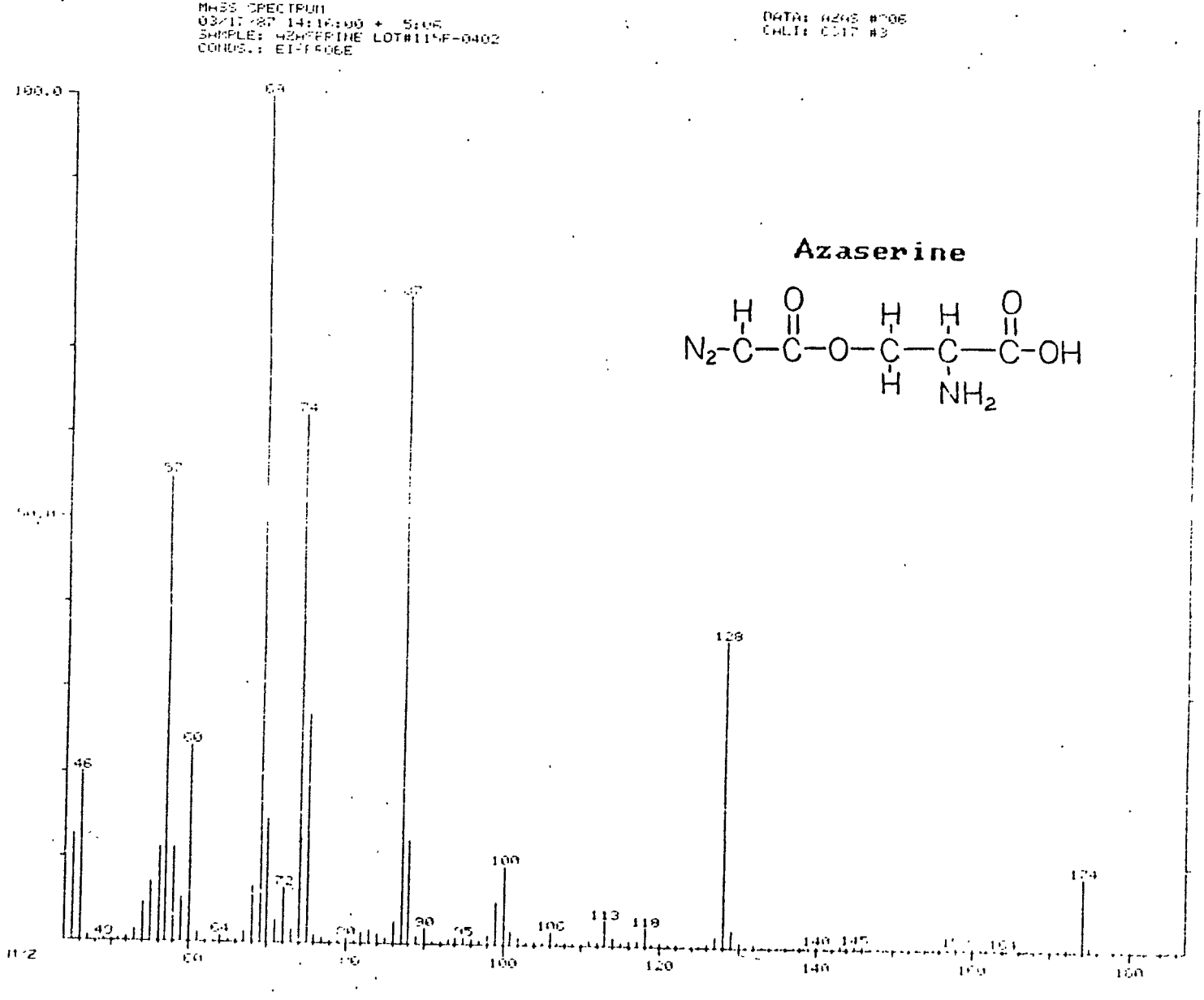
(CH3)2 N–C–S–S–C–N(CH3)2
S
S

MASS SPECTRUM
02 10/87 14:27:00 + 2:15
SAMPLE: METHYL METHACRYLATE LOT#01G2EHP
COND .: EI
GC TEMP: 50 DEG. C

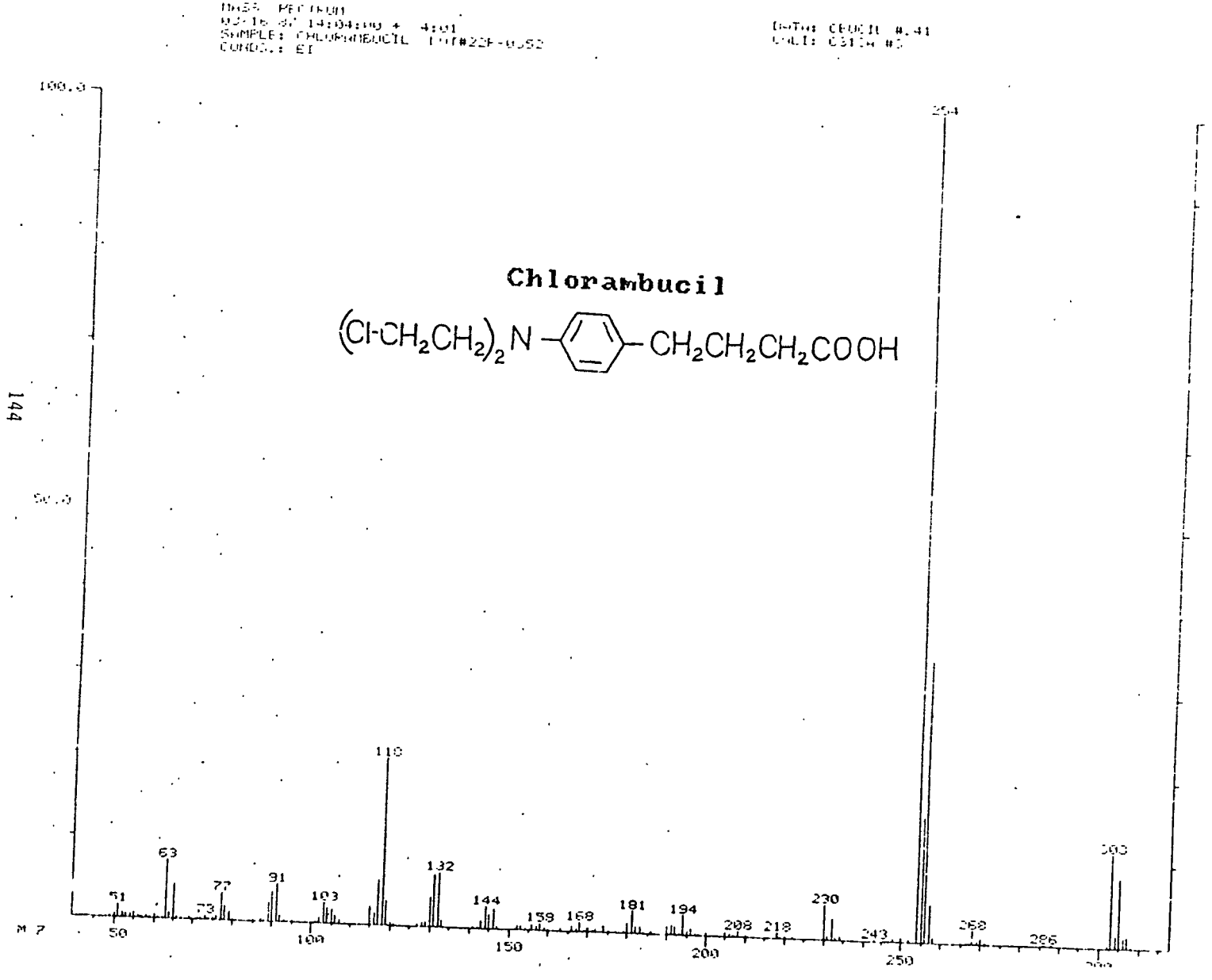
DATA: MEME #135
CALI: C317 #3

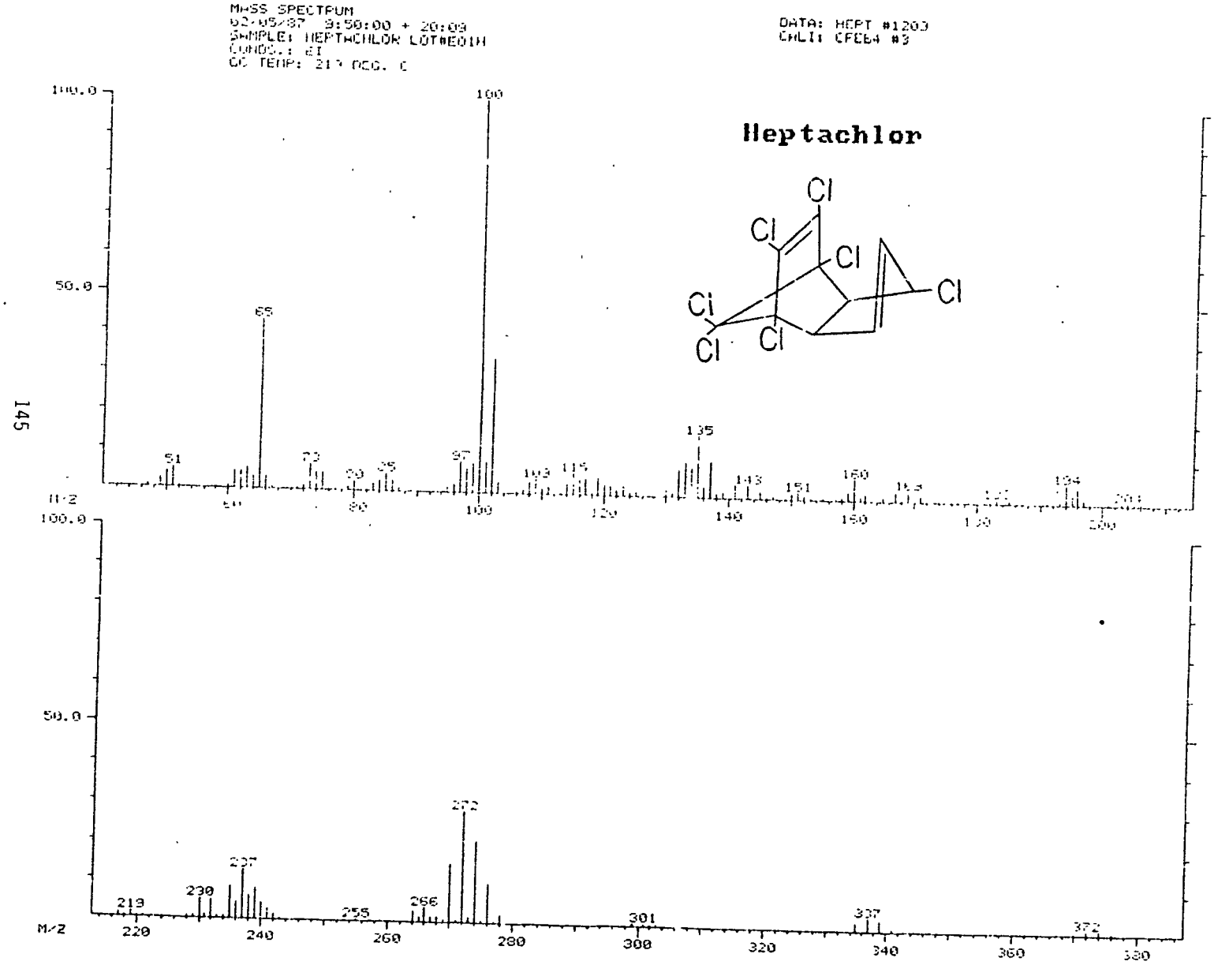


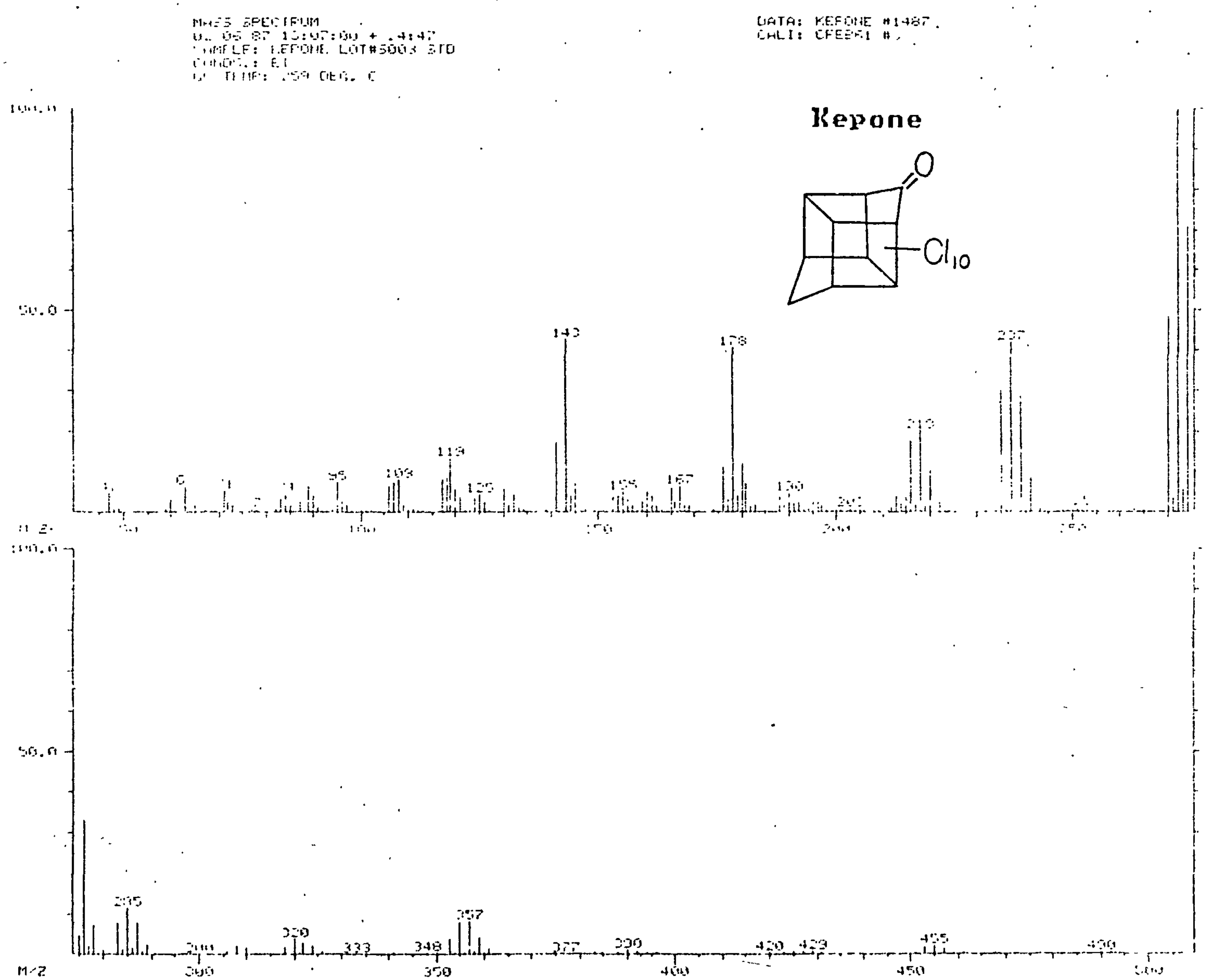
Methyl Methacrylate


MASS SPECTRUM
03/17/87 14:16:00 + 5:05
SAMPLE: AZASERINE LOT#115F-0402
CONDS.: EI-FS06E
DATA: AZAS #206
CALI: C017 #3
100.0
m/z
64
57
74
87
46
60
72
42
54
80
90
95
100
105
113
118
128
140
145
154
120
140
160

Azaserine


Chlorambucil
$(Cl\text{-}CH_2CH_2)_2N$ — $CH_2CH_2CH_2COOH$
144
M/Z
50
100
150
200
250
63
77
91
103
110
132
144
159
168
181
194
208
218
230
243
254
268
286
303


MASS SPECTRUM
02/05/87 9:50:00 + 20:09
SAMPLE: HEPTACHLOR LOT#E01H
COMDS.: EI
GC TEMP: 217 DEG. C
DATA: HEPT #1203
CHLI: CFEB4 #3
Heptachlor
Cl
Cl
Cl
Cl
Cl
Cl
100.0
50.0
145
100
65
51
73
50
95
97
135
193
115
143
151
160
194
201
M/Z
100.0
50.0
272
237
230
213
255
266
301
337
372
M/Z


MASS SPECTRUM
SAMPLE: KEPONE LOT#5003 STD
CONDS.: EI
DATA: KEPONE #1487
Kepone
O
Cl10
100.0
50.0
143
178
237
119
103
95
129
167
213
M/Z
300
350
400
450
295
320
333
348
357
377
390
420
429
455
490

APPENDIX B

FT-IR ANALYSIS

The identities of three of the "second third" compounds (methyl methacrylate [MM], O,O,O-triethylester phosphorothioic acid [OP], and tris(2,3-dibromopropyl)-phosphate [Tris]) were confirmed by their infrared spectra. A Digilab FTS-20C Fourier transform infrared instrument with a glowbar source and a MCT detector were used for this purpose. In each case, spectra were obtained as a thin film between KBr disks. Figures B1 and B2 are the spectra of MM and OP, respectively. In both cases, the spectra match very well with standard reference spectra to give acceptable confirmation of MM and OP. Additionally, Figure B3, which is a spectrum of Tris, matches well with the standard reference spectrum. There was some concern as to whether Tris could possibly be the tris(1,3-dibromo-2-propyl)phosphate isomer, for which no standard reference spectrum could be located. This possibility was essentially eliminated by recording the spectra of 2,3-dibromo-1-propanol (Figure B4) and 1,3-dibromo-2-propanol (Figure B5). Since the C-H bands (at 3000 and 1500 cm^{-1}) of the two alcohols are quite different, and the C-H bands of Tris closely match those of 2,3-dibromo-1-propanol, the structure of Tris was confirmed.

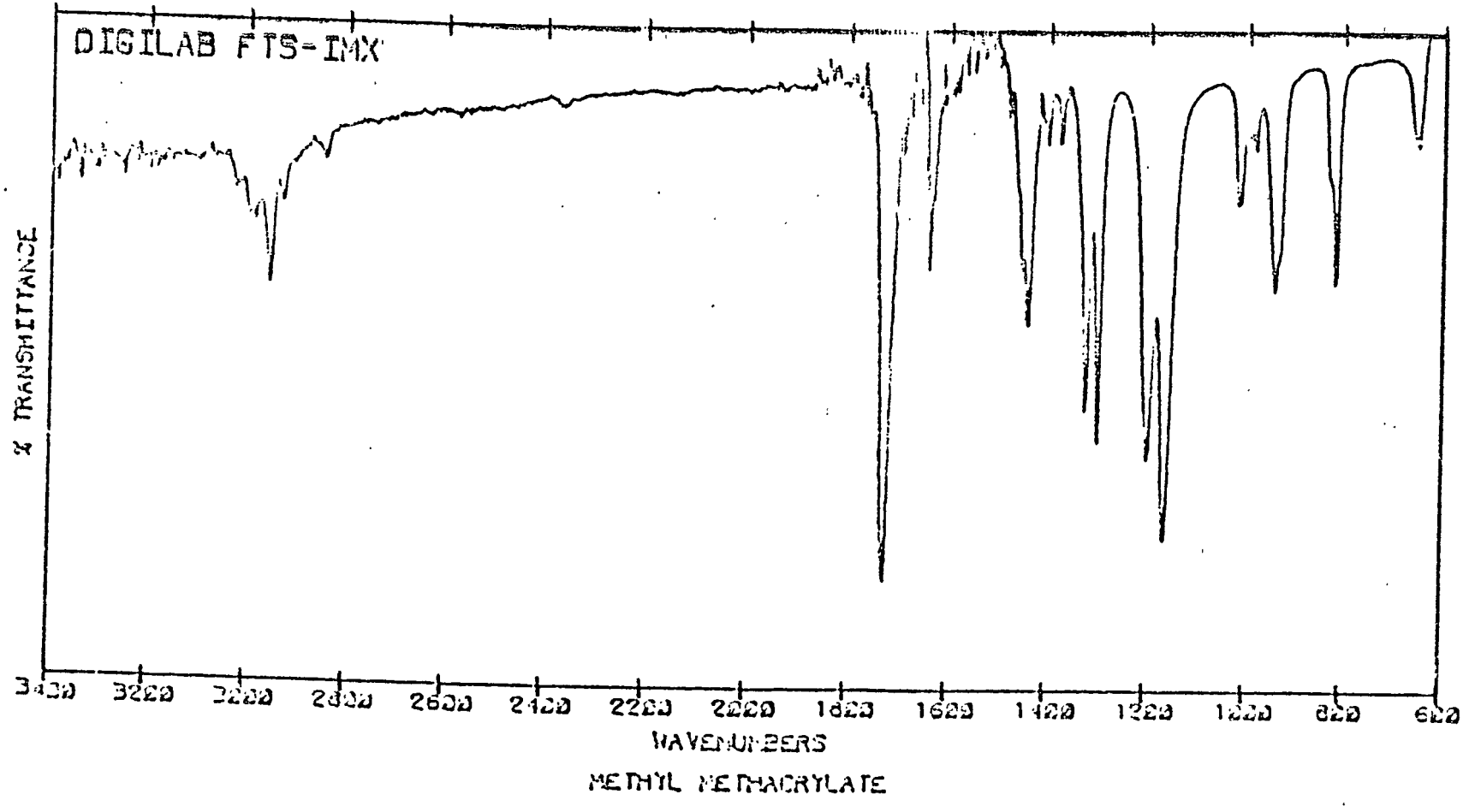


Figure B1. Infrared Spectra of Methyl Methacrylate

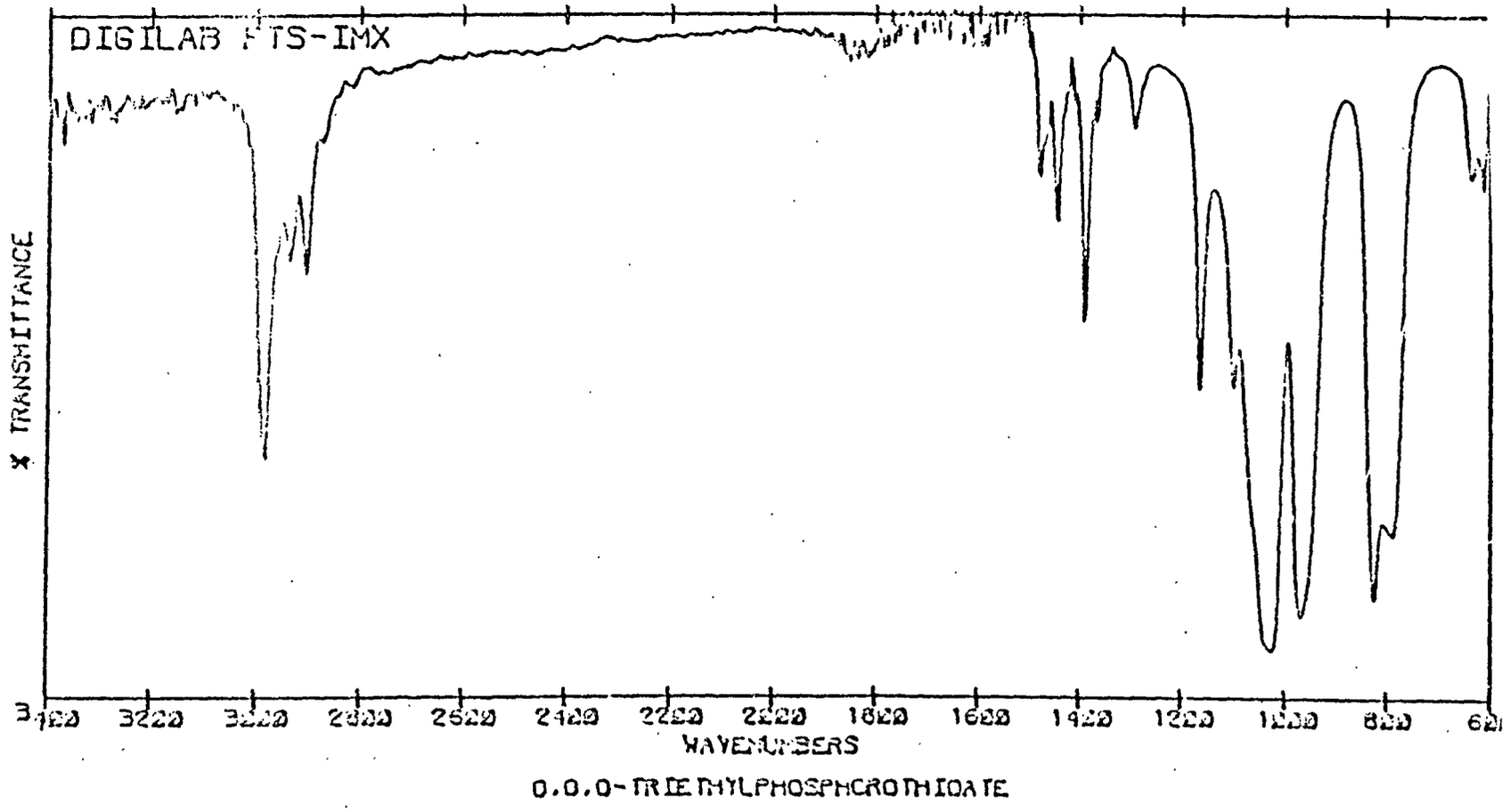


Figure B2. Infrared Spectra of 0.0,0-Triethylester Phosphorothioic Acid

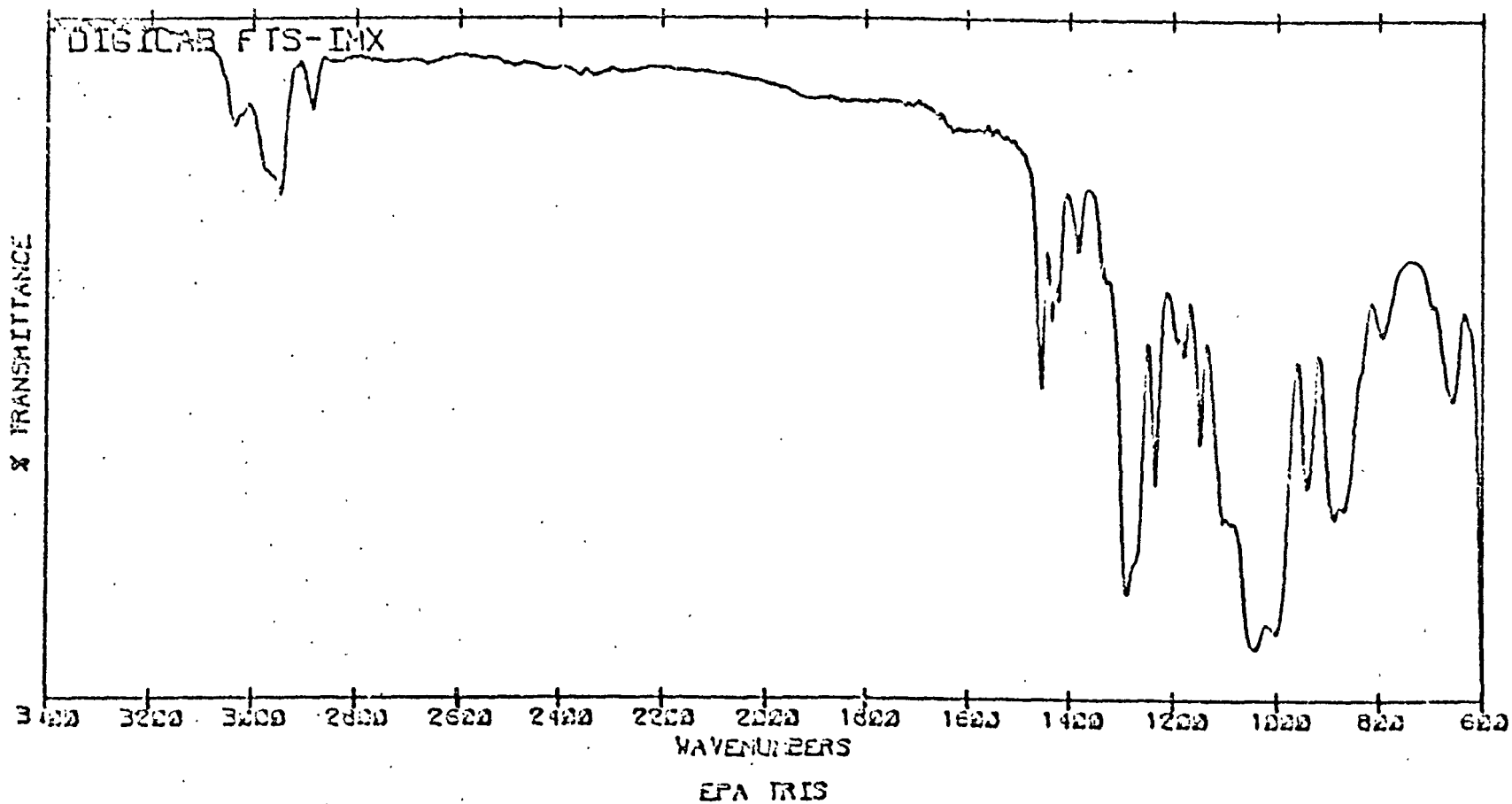


Figure B3. Infrared Spectra of Tris(2,3-Dibromopropyl)Phosphate

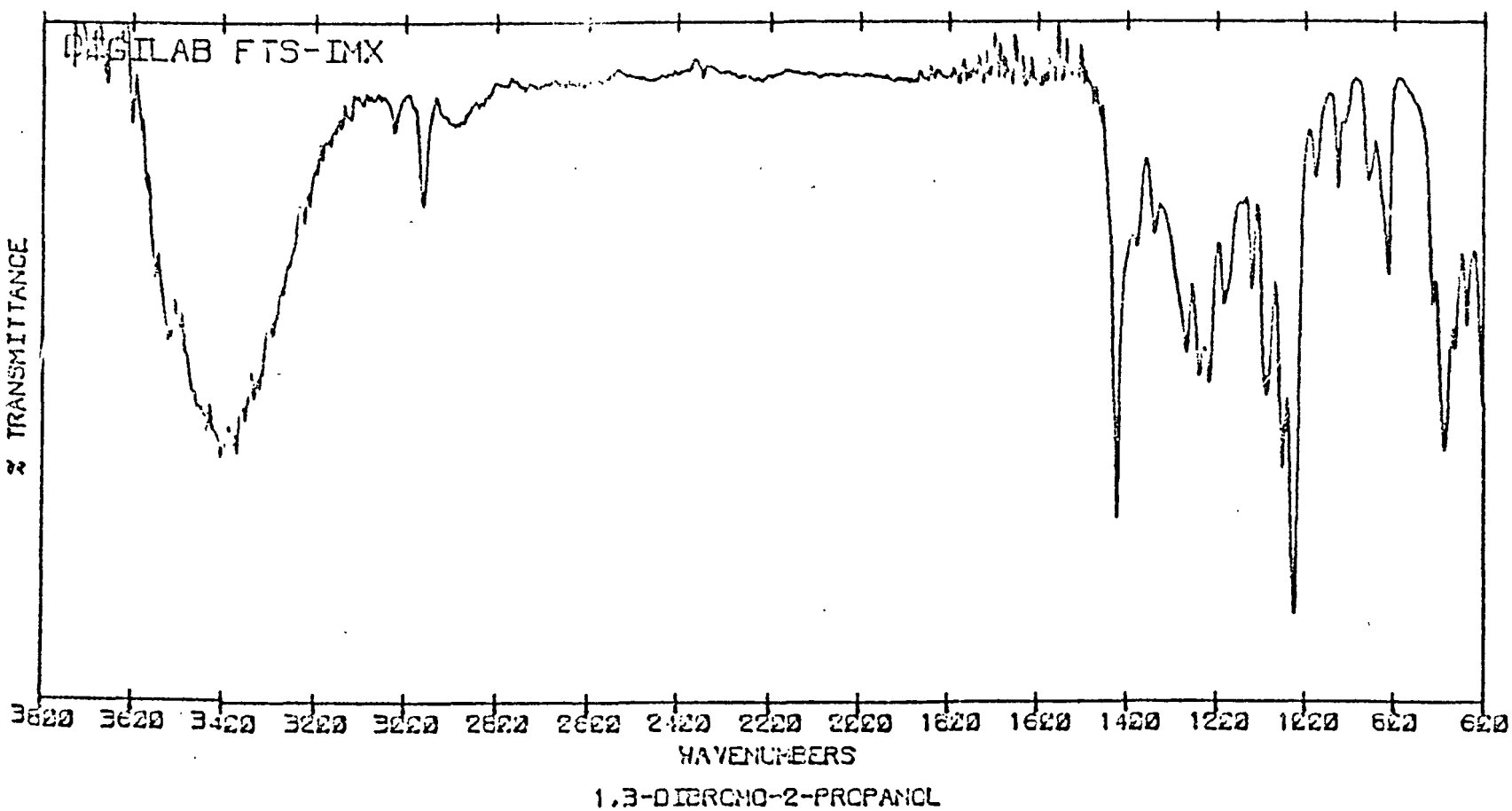


Figure B5. Infrared Spectra of 1,3-Dibromo-2-Propanol

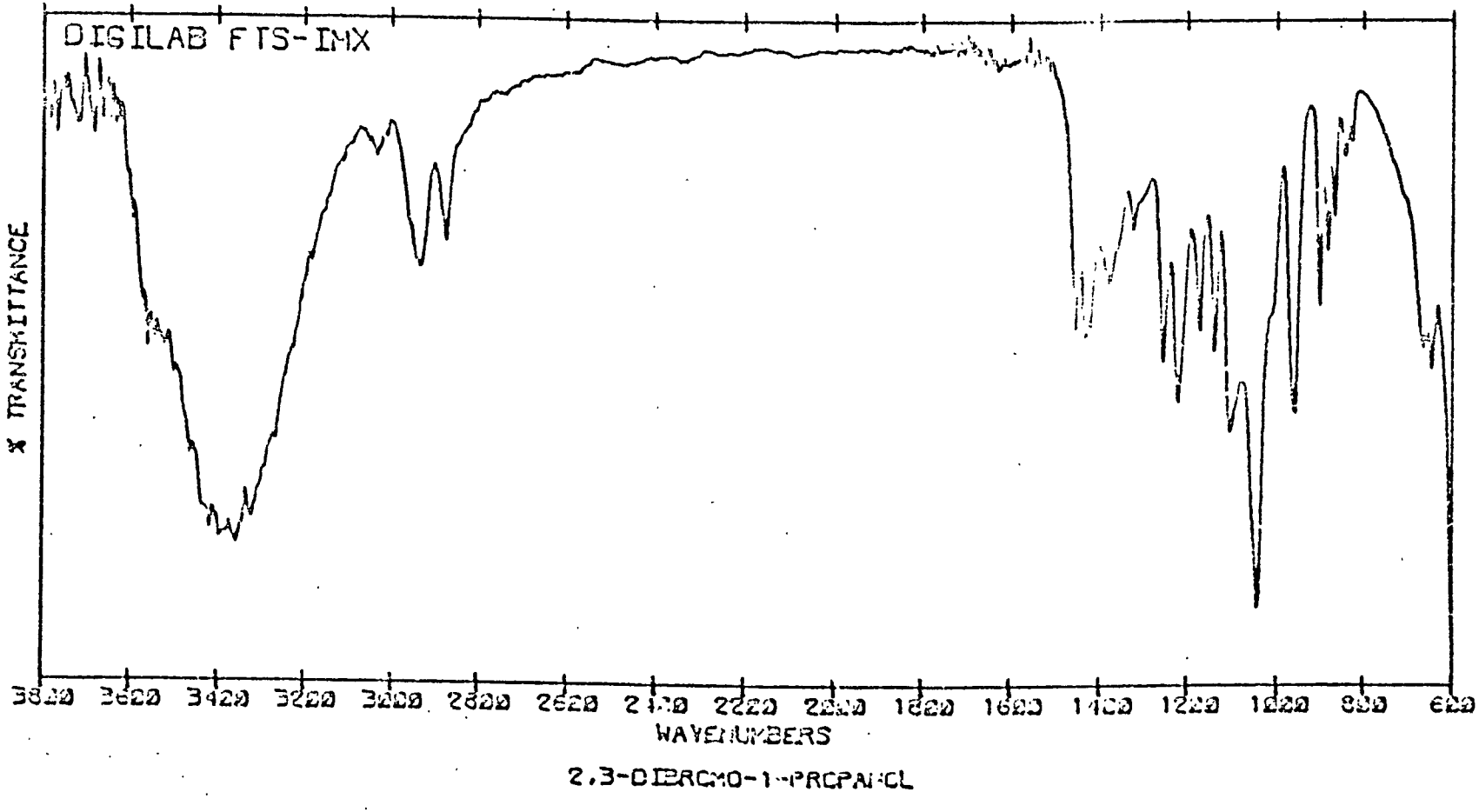


Figure B4. Infrared Spectra of 2,3-Dibromo-1-Propanol

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