

Analysis of Decomposition Products of Pesticides

Maurice V. Kennedy,* Boris J. Stojanovic, and Fred L. Shuman, Jr.

Analyses were conducted to identify the products formed upon chemical or thermal decomposition of 20 selected pesticides. The gaseous products resulting from heat treatment were analyzed by gas chromatography, infrared spectra, adsorption onto solids, or absorption into liquids. The wide variety of products made it necessary to employ electron capture, hydrogen flame ionization, and thermal conductivity detectors for the gas chromatographic analyses. Thermal decomposition products occurring were carbon dioxide, carbon monoxide,

nitrogen oxides, hydrochloric acid, and residues of inorganic compounds. Analyses performed to determine the decomposition products when the pesticides were exposed to chemicals gave a variety of compounds, depending on the chemical used. The decomposition product(s), if any, is identified for certain of the pesticides after exposure to the potential decontaminants. These products include compounds formed by oxidation, reduction, molecular structure rearrangement, and decomposition.

The disposal of waste pesticides and pesticides containers without contaminating the environment is one of the major problems of today. It is compounded by the wide variety of chemicals which are used as pesticides, making it difficult to develop a single method of disposal which can be universally employed.

Enzymatic action, hydrolysis, or the action of soil microorganisms may degrade small quantities or weak solutions of certain pesticides. However, these decomposition processes proceed slowly and are not practical for large quantities of materials.

Two of the most promising methods investigated thus far for disposal of waste pesticides has been chemical reactions and incineration. These methods have the advantages of being rapid and, in the case of incineration, effecting complete destruction. However, decomposition of pesticide chemicals by either of these methods produces degradation products which could be potentially as hazardous as the original compound. The present investigation deals with the detection and analysis of breakdown products resulting from chemical reaction or combustion of pesticides.

EXPERIMENTAL

Methods. A modified pyrolysis method was chosen to determine the volatile products of incineration. The process was modified by the introduction of air into the pyrolysis chamber, which in effect converted it to a combustion chamber. This was done to simulate as nearly as possible the conditions which might be present in an incinerator.

A temperature of 900°C was chosen for burning. This is sufficiently high to decompose any of the 20 pesticidal compounds investigated by Kennedy *et al.* (1969). This temperature is also easily attainable by most commercial incinerators presently on the market.

The simulated incineration was carried out using a commercial pyrolyzer equipped with a nickel ribbon heating element. The pyrolysis chamber was flushed with air and the compounds burned in the air atmosphere. Standard gases (Matheson Scientific Co.) were analyzed and the resulting gaseous products identified by retention time.

The infrared analyses were performed on a Perkin-Elmer Model 337 grating infrared spectrophotometer using a KBr micropellet and a beam condenser or a pair of liquid cells with KBr windows. Extractions of the reacted compounds

were made and carbon tetrachloride, chloroform, or ethanol was used as the solvent for liquid determinations.

The pesticidal compounds were reacted directly with the potential decontaminants in a 5:1 decontaminant to pesticide ratio, unless otherwise stated. The compound was placed in either a glass stoppered Erlenmeyer flask or a test tube for reaction. Certain of the compounds were reacted at elevated temperatures by placing the reaction vessels on an electric hot plate.

Materials Studied. Analytical standards of 20 pesticide chemicals were used in the present study. These were:

- Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine)
- Bromacil (5-bromo-3-*sec*-butyl-6-methyluracil)
- Carbaryl (1-naphthyl *N*-methylcarbamate)
- Dalapon (2,2-dichloropropionic acid)
- DDT (2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane)
- Dicamba (2-methoxy-3,6-dichlorobenzoic acid)
- Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a - octahydro - 1,4 - *endo,exo* - 5,8 - dimethanonaphthalene)
- Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]
- DNBP (4,6-dinitro-*o*-*sec*-butyl phenol)
- DSMA (disodium methanearsonate)
- Malathion (*O,O*-dimethyl dithiophosphate of diethyl mercaptosuccinate)
- Nemagon (1,2-dibromo-3-chloropropane)
- Paraquat (1,1'-dimethyl-4,4'-bipyridinium)
- Picloram (4-amino-3,5,6-trichloropicolinic acid)
- PMA (phenylmercuric acetate)
- Trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine)
- 2,4-D (2,4-dichlorophenoxyacetic acid)
- 2,4,5-T (2,4,5-trichlorophenoxyacetic acid)
- Vernam (*S*-propyl dipropylthiocarbamate)
- Zineb (zinc ethylenebisdithiocarbamate)

Apparatus. A thermal conductivity detector which was attached to a Barber-Colman Model 5000 gas chromatograph was employed. This unit was equipped with two matched pairs of Gow-Mac tungsten-rhenium filaments. The gas chromatographic column was packed with an 80-100 mesh porous polymer bead packing (Poropak Q, Waters Associates, Framingham, Mass.) (Hollis, 1966) and was 6 ft in length. Nitrogen was employed as the carrier gas. A Barber-Colman Model 5180 pyrolyzer was attached to the gas chromatograph and was used as a modified combustion chamber for the pesticides. This unit contained a nickel ribbon with variable control of the temperature from 100 to 1100°C. This unit had capability for operation manually or automatically.

Mississippi State University, State College, Mississippi 39762.

Table I. Volatile Products from Burning of Analytical Grade Pesticides at 900°C

Pesticide	Peaks identified	Peaks unidentified
Atrazine	CO, CO ₂ , Cl ₂ , HCl, NH ₃	3.8-13.7-14.4
Bromacil	CO, CO ₂	3.0-9.5
Carbaryl	CO, CO ₂ , NH ₃ , O ₂	3.0-17.0
Dalapon	CO, CO ₂ , Cl ₂ , O ₂ , HCl	18.0
DDT	CO, CO ₂ , Cl ₂ , HCl	9.4
Dicamba	CO, CO ₂ , Cl ₂ , HCl, O ₂	1.2-16.7
Dieldrin	CO, CO ₂ , Cl ₂ , HCl, O ₂	1.1
Diuron	CO, CO ₂ , Cl ₂ , NO, HCl, NH ₃	1.4
DNBP	CO, CO ₂ , NH ₃	3.9-16.2
DSMA	CO, CO ₂ , O ₂	3.8-4.8
Malathion	CO, CO ₂ , SO ₂ , H ₂ S, O ₂	3.5-4.5-14.2-17.5
Nemagon	CO, CO ₂ , Cl ₂ , HCl	4.0-9.5-13.6-19.2
Paraquat	CO, CO ₂ , NH ₃	4.0-16.5
Picloram	CO, CO ₂ , Cl ₂ , NH ₃	11.0-17.0
PMA	CO, CO ₂	3.8-4.8
Trifluralin	CO, CO ₂ , NH ₃	3.0-4.0-13.8-16.8
2,4-D	CO, CO ₂ , Cl ₂ , HCl, O ₂	None
2,4,5-T	CO, CO ₂ , Cl ₂ , HCl, O ₂	None
Vernam	CO, CO ₂ , NH ₃ , O ₂	2.8-3.6-13.2-15.0-16.8
Zineb	CO, CO ₂ , H ₂ S, NH ₃	4.0-17.2

Relative retention time: CO, 1 (48 sec); CO₂, 2.0; Cl₂, 2.1; NO, 2.2; SO₂, 2.3; HCl, 3.2; H₂S, 5.8; NH₃, 9.0; O₂, 10.0. Column: 6 ft glass, Porapak Q. Thermal conductivity detector.

Table II. Recovery of Carbon Dioxide from Combustion of Analytical Grade Pesticides at 900°C

Pesticide	Percentage carbon		
	Calculated	Determined	Accounted for
Atrazine	44.5	31.8	71.5
Bromacil	41.4	35.4	85.5
Carbaryl	71.5	65.4	91.5
Dicamba	43.2	37.9	87.7
Dieldrin	37.4	26.5	97.6
Diuron	46.3	35.5	76.7
DNBP	49.5	47.4	95.8
Paraquat	46.0	37.4	66.8
Picloram	29.5	26.9	91.2
2,4-D	43.4	41.6	95.9

Thin-layer chromatography (Walker and Beroza, 1963) and infrared analysis (Sadler Index, 1966) were used to determine the effect of treatment on the pesticides.

Certain of the analyses were performed using a Microtek 220 gas chromatograph equipped with an electron capture detector and a hydrogen flame ionization detector. Nitrogen was employed as the carrier gas.

A selected number of the pesticidal compounds were analyzed by dry combustion to check for the quantity of CO₂ produced upon burning against the total amount of carbon in the compounds. The method used was a modified version of that employed by Allison *et al.* (1965). It involved the burning of the pesticide at 900°C for 15 min in a resistance type furnace in a stream of purified oxygen and the absorption of the carbon dioxide in the effluent gas stream by ascarite. The evolved carbon dioxide was determined gravimetrically. A plug of platinized asbestos which served as catalyst was inserted in the combustion tube at the rear of the heated zone to insure complete oxidation of the carbon monoxide to carbon dioxide. The sample was heated by radiation, conduction, and convection in a tube surrounded by heating elements made of high resistance material. Gaseous products of thermal breakdown of organic molecules other than carbon dioxide,

which would also be absorbed and could introduce a large error in estimating the CO₂ were removed from the air stream. The purification system used to free the incoming and outgoing stream of oxygen was as follows. Concentrated sulfuric acid was used to trap ammonia, hydrocarbons, and water vapor; activated MnO₂ was used to absorb nitrogen and sulfur oxides and halogens; magnesium perchlorate was used to pick up water vapor; and ascarite was used to absorb the carbon dioxide.

Reagents and Solvents. The developing solvent systems for thin-layer chromatography were benzene-*n*-hexane (1:1) and benzene-acetone (9:1). The developed plates were exposed to bromine vapor (5% v/v Br in CCl₄) and the vapor was allowed to evaporate. Finally they were sprayed with fluorescein made up as 0.25% w/v in dimethylformamide and diluted (1:50) with 25% ethanol. Plates carrying chlorinated hydrocarbons were also sprayed with AgNO₃ solution (1.7 g of AgNO₃ in 5 ml of distilled water to which 20 ml of 2-phenoxyethanol was added and diluted to 200 ml with acetone). The plates were then exposed to uv light for 5 to 7 min and the spots circumscribed.

The solvents used for gas chromatography were chemically pure grade and were redistilled from glass in our own laboratory.

RESULTS AND DISCUSSION

The modified pyrolysis-combustion procedure produced information which is very useful in identifying gaseous products resulting from burning of pesticides.

Beroza and Coad (1966) gave a very excellent review of pyrolysis procedures and applications. Arbitrary grouping of pyrolyses were made based on temperature employed and extent of degradation. A temperature of 900°C was employed in the present investigation which falls into the highest temperature group called vigorous pyrolysis.

A wide variety of gaseous products may be expected from the burning of pesticidal compounds at the temperature utilized. One may note from Table I that, as expected, all of the compounds produced CO and CO₂ upon burning. However, by utilizing pure oxygen in a combustion apparatus (Table II), most of the total carbon present in analytical grade pesticides was accounted for as carbon dioxide. One would assume that in this case, with a large excess of oxygen, all of the CO produced would be oxidized to CO₂. The remainder of the carbon may be accounted for by the formation of traces of other carbon gases such as HCN. One would expect that hydrogen bromide would be produced from the burning of Bromacil; however, this gas was not detected, even though specific analyses were made for its presence.

One must also point out, too, that changing of conditions would produce changes in the resulting volatile products. For instance, the degradation products would be dependent upon the temperature, the duration of heating, the atmosphere, the carrier gas, the stability of the compound, and several other variables.

The compounds in the present investigation, with the conditions utilized, produced at least two gases containing chlorine. These were hydrogen chloride and elemental chlorine gas. With a sufficiently reducing atmosphere it is quite possible that much of the elemental chlorine gas would be converted to hydrogen chloride. This would facilitate the recovery and removal of this gas by the entrainment through aqueous media.

Sulfur dioxide and hydrogen sulfide were produced from two of the sulfur-bearing compounds. The assumption may

be made that sulfur gases would be produced from the burning of any pesticide containing sulfur, but should present no real difficulty for removal from the effluent gas stream.

Gaseous products of nitrogen which were detected consisted mostly of ammonia. Some difficulty was experienced in separation of the nitrogen oxides, although nitric oxide was determined as one of the gases produced from the burning of Diuron. A cold temperature (-78°C) was employed for the gas chromatographic column, but attempts to separate and identify the other nitrogen oxides, if any, were unsuccessful.

The treatment of pesticides with chemicals to produce degradation was not 100% effective in any case. From the data obtained the assumption can be made that only a few of the compounds would approach complete degradation, even if the solutions were composed of weaker concentrations. And since the ultimate objective of the research is to produce an effective acceptable method for the disposal of waste pesticides, one would only be enlarging the total volume by diluting the compounds. However, if this produced an efficient economical method for disposal, then the ultimate end would be served. Indications are that dilution of the compounds would not enhance total degradation appreciably.

Data resulting from chemical treatment of pesticides are presented in Table III. It may be noted that atrazine, carbaryl, and malathion were partially decomposed when treated with ammonium hydroxide. Sulfuric acid was effective in bringing about changes in Bromacil, Dicamba, DSMA, 2,4-D, 2,4,5-T, Vernam, and Zineb. However, sulfuric acid did not produce any changes in Picloram. This is not remarkable since one would expect that compounds of quite unrelated structure would not necessarily be degraded by similar pathways.

Sodium hydroxide was effective in producing structural changes in DDT, Diuron, DNBP, Malathion, Trifluralin, 2,4-D, 2,4,5-T, and Vernam. Indications were that only small changes were evident in seven of these compounds; however, inorganic phosphate was produced from Malathion.

Calcium hypochlorite was the most nearly universal decontaminant in producing structural changes in a wide range of compounds. However, even this was not completely effective in decomposing the treated pesticides.

The results of the research conducted indicate that burning of pesticides will produce some potentially hazardous gases. However, all of the harmful volatile products which have been identified can be removed from the effluent gas stream by the employment of proper scrubbers. Conditions can possibly be achieved which will help to eliminate or convert some of the undesirable gases.

Chemical treatment was not totally effective in decomposing pesticides in any case. The wide range of molecular structures which makes up the broad spectrum of pesticides will make it difficult if not impossible to discover a single agent which will be effective universally. Certain of the compounds were partially degraded by chemical reaction which is encouraging for potential use with certain classes of compounds.

Table III. Chemical Treatment of Pesticides

Pesticide	Chemical agent	Reaction of products
Atrazine	15 N NH_4OH	2-Chloro compound
Bromacil	18 N H_2SO_4	Partially decomposed
Carbaryl	16 N HNO_3	Nitrobenzene
	15 N NH_4OH	1-Naphthol
Dalapon	16 N HNO_3	Partially decomposed
DDT	8 N NaOH	Partially decomposed
	100% TEA	Partially decomposed
Dicamba	8 N NaOH	Unchanged
	18 N H_2SO_4	Partially decomposed
	70% $\text{Ca}(\text{ClO})_2$	Partially decomposed
	100% MEA ^a	Unchanged
	100% TEA ^b	Unchanged
Dieldrin	30% H_2O_2	Partially decomposed
	100% MEA	Unchanged
Diuron	70% $\text{Ca}(\text{ClO})_2$	Partially decomposed
	8 N NaOH	Partially decomposed
DNBP	70% $\text{Ca}(\text{ClO})_2$	Partially decomposed
	8 N NaOH	Partially decomposed
DSMA	18 N H_2SO_4	Arsenic
	100% TEA	Unchanged
Malathion	8 N NaOH	Inorganic phosphate
	15 N NH_4OH	Partial decomposition
	100% TEA	Unchanged
Nemagon	100% MEA	Unchanged
Paraquat	100% MEA	Unchanged
Picloram	8 N NaOH	Unchanged
	18 N NaOH	Unchanged
PMA	100% MEA	Unchanged
Trifluralin	30% H_2O_2	Partial decomposition
	8 N NaOH	Partial decomposition
2,4-D	70% $\text{Ca}(\text{ClO})_2$	Partially decomposed
	8 N NaOH	Partially decomposed
	18 N H_2SO_4	Partially decomposed
2,4,5-T	8 N NaOH	Partially decomposed
	18 N H_2SO_4	Partially decomposed
Vernam	8 N NaOH	Partially decomposed
	18 N H_2SO_4	Partially decomposed
Zineb	18 N H_2SO_4	Hydrogen sulfide, free zinc
	100% TEA	Unchanged

^a Monoethanolamine. ^b Triethanolamine.

LITERATURE CITED

- Allison, L. E., Bollen, W. B., Moodie, C. D., Total Carbon, In "Methods of Soil Analysis," Part 2, *Agronomy Monograph No. 9*, American Society of Agronomy, Inc., Madison, Wisconsin (1965).
 Beroza, M., Coad, R. A., *J. Gas Chromatogr.* **4**, 199 (1966).
 Hollis, O. L., *Anal. Chem.* **38**, 309 (1966).
 Kennedy, M. V., Stojanovic, B. J., Shuman, Jr., F. L., *Residue Rev.* **29**, 89 (1969).
 Sadtler Index, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania (1966).
 Walker, K. C., Beroza, M., *J. Ass. Offic. Anal. Chem.* **46**, 250 (1963).

Received for review February 19, 1971. Accepted October 26, 1971. Contribution from the Mississippi Agricultural and Forestry Experiment Station, Mississippi State University, State College, Miss. This study was supported by Agricultural Research Service, U.S. Department of Agriculture, Grant No. 10-12-14-100-9182 (34), administered by the Crops Research Division, Beltsville, Md. Mention of proprietary products is for identification only and does not constitute nor imply endorsement by the Mississippi Agricultural and Forestry Experiment Station nor the United States Department of Agriculture.