

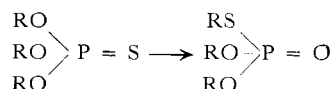
Thermal Decomposition of Some Phosphorothioate Insecticides

JAMES B. McPHERSON, Jr.,
and GERALD A. JOHNSON

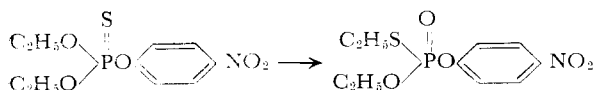
Agricultural Chemicals Section,
Product Research Department,
American Cyanamid Co.,
Stamford, Conn.

Explosive decomposition of a pilot plant batch of the methyl homolog of parathion, which occurred as a result of accidental overheating while the solvent was being removed by distillation, led to study of the nature of the decomposition and to "stable life" determinations of parathion, its methyl homolog, Insecticide 4124, Chlorothion, and malathion at normal operating temperatures. Decomposition of the methyl homolog of parathion occurs in two steps, the first of which generates dimethyl sulfide, sulfur dioxide, and a mixture indicated to contain mixed poly(aryl metaphosphates). This mixture decomposes, sometimes explosively, to a carbonaceous residue in the second step. Estimated times for decomposition to occur are given for the 65° to 115° C. range.

THE ISOMERIZATION OF ALKYL PHOSPHOROTHIOATES under the influence of heat has long been known to those who work in the field of organic phosphorus compounds. In 1911 Emmett and Jones (4) reported the isomerization of *O,O,O*-trimethyl phosphorothioate and the corresponding triethyl ester.



Schrader (2) described a similar reaction for parathion, which occurred when the insecticide was heated at 130° to 140° C. or more.



The same reaction served as the basis for a patent granted to Morrill (9), covering a process for preparing the *S*-ethyl isomer of parathion, a compound described as having "greatly enhanced insecticidal activity." In this process, parathion, on being heated at 160° to 170° C. for 10 hours, is reported to undergo nearly quantitative conversion to the *S*-ethyl isomer.

It has been shown by Diggle and Gage (3) that purified parathion is a feeble inhibitor of cholinesterase *in vitro*, and that the *in vitro* activity increases with increasing concentration of the *S*-ethyl isomer.

Numerous other workers have compared the toxicities of parathion and its isomer, both to insects and to mammals, with varying results. In most cases the *S*-ethyl isomer of parathion, although toxic, has shown less toxicity toward insects than parathion itself, in spite of its higher *in vitro* anticholinesterase activ-

ity. Conflicting results have been obtained in comparing the mammalian toxicities of the two isomers. These studies have been summarized by Metcalf and March (8), who extended the research to include a comparison of the toxicities of malathion, EPN (*O*-ethyl *O*-*p*-nitrophenyl phenylphosphonothioate), and the methyl and isopropyl homologs of parathion, as well as parathion itself, with the toxicities of the corresponding *S*-alkyl isomers.

Several workers have indicated that heat treatment of parathion and similar compounds can lead not only to isomerization but to decomposition.

Martin (7) observed a progressive decrease in toxicity toward *Calandra granaria* as parathion was heated at 150° C. for 24 hours. A similar reduction in toxicity toward the same insect occurred

when the methyl homolog of parathion was heated for 6 hours at the same temperature. In both cases thiono sulfur content diminished to practically nothing during the heating period. The author commented that "the absence of contact toxicity of the compounds when heated to zero thiono sulfur content would indicate that heat treatment leads to changes more extensive than isomerization."

In a paper in which the vapor pressures of parathion, its *S*-ethyl isomer, and other phosphorothioates were reported, Bright, Cuthill, and Woodbury (7) commented that the distillation of parathion under vacuum at temperatures greater than 100° C. is "a hazardous procedure which frequently results in violent decomposition."

Topley (13) reported that "the isomerization (of parathion) is later accompanied by an autocatalytic decomposition in which acidic substances are produced."

Woodcock and Stringer (15) confirmed the isomerization of both parathion and its methyl homolog at temperatures above 140° C. and noted also that further heating of the *S*-ethyl isomer of parathion resulted in thermal decomposition and loss of toxicity to *C. granaria*. In their studies pure parathion was heated at 150° C. for 18 hours, which reduced the thiono sulfur content to zero. When heating was continued for an additional 15 hours, an extremely viscous black material remained. Moreover, when *O,S*-diethyl *O*-(*p*-nitrophenyl) phosphorothioate was heated for 15 hours at 150° C. there was formed a dark and viscous product which was insoluble in acetone.

Metcalf and March (8) described the thermal decomposition products of some of the phosphorothioate insecticides with more detail than had the previous authors. When the methyl homolog of parathion was heated for 3.5 hours at 150° C., there was formed a yellowish viscous liquid with a pronounced mercaptan-like odor. Heating at the same temperature for 24 hours or longer produced two phases which were described as a very volatile, mobile liquid and a muddy solid. The isopropyl homolog of parathion, on being heated for 3 hours at 150° C., similarly yielded a mobile liquid and a brownish, highly viscous material. Two phases, an orange-brown viscous liquid and some colorless cloudy material, were also obtained when malathion was heated at 150° C. for 24 hours.

Chromatographic studies conducted by Metcalf and March indicated the presence of eight compounds following the heat treatment (24 hours at 150° C.) of purified parathion, five of which were tentatively identified as:

1. *O*-Ethyl *O,O*-bis(*p*-nitrophenyl)-phosphorothioate

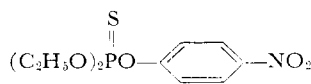
2. Parathion
3. *O,S*-Diethyl *O*-(*p*-nitrophenyl) phosphorothioate
4. Diethyl *p*-nitrophenyl phosphate
5. *p*-Nitrophenol

The remaining three compounds, which were observed by chromatographic separation, were of unknown structure.

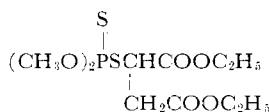
A similar chromatographic analysis conducted on the heat-treated methyl homolog of parathion (6 hours at 150° C.) indicated the presence of four compounds: two tentatively identified as *O,S*-dimethyl *O*-(*p*-nitrophenyl) phosphorothioate and dimethyl *p*-nitrophenyl phosphate, and two of unknown structure. Additional evidence of decomposition was seen in the fact that the heat-treated material was not completely soluble in acetone.

Thus, there has been evidence in the literature that, under the influence of heat, certain phosphorothioates will not only isomerize, but will also undergo some kind of decomposition.

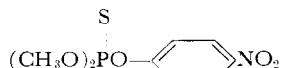
A study of this decomposition was undertaken in these laboratories to learn something of its course, and primarily to determine conditions under which decomposition could be avoided at temperatures used during the synthesis of the following phosphorothioate insecticides.



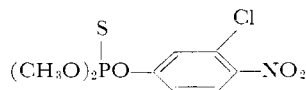
Parathion



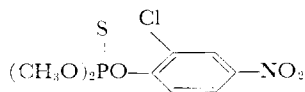
Malathion



Methyl Homolog of Parathion



Chlorothion



Insecticide 4124

Materials Used

The *O,O*-dimethyl *O*-(*p*-nitrophenyl) phosphorothioate (methyl homolog of parathion) used for many of these studies was a white, crystalline solid, melting at 36.6–37.1° C. (corr.). Its purity was indicated to be 99.5% or better by the constant temperature differential cryoscopic method (14), and 100% by the method of O'Keeffe and Averell (17). Analysis. Calculated for C₈H₁₀NO₅PS: nitrogen, 5.32; phosphorus, 11.77; sulfur, 12.18. Found: nitrogen, 5.30; phosphorus, 11.50; sulfur, 12.90.

The *O,O*-diethyl *O*-(*p*-nitrophenyl) phosphorothioate (parathion) used was a colorless liquid freezing at 5.95° ± 0.05° C. and having a purity of 99.8% (O'Keeffe and Averell procedure).

The *S*-(1,2-dicarboethoxyethyl) *O,O*-

dimethyl phosphorodithioate (malathion), a colorless liquid, was 100% pure by both polarographic (6) and colorimetric (10) procedures.

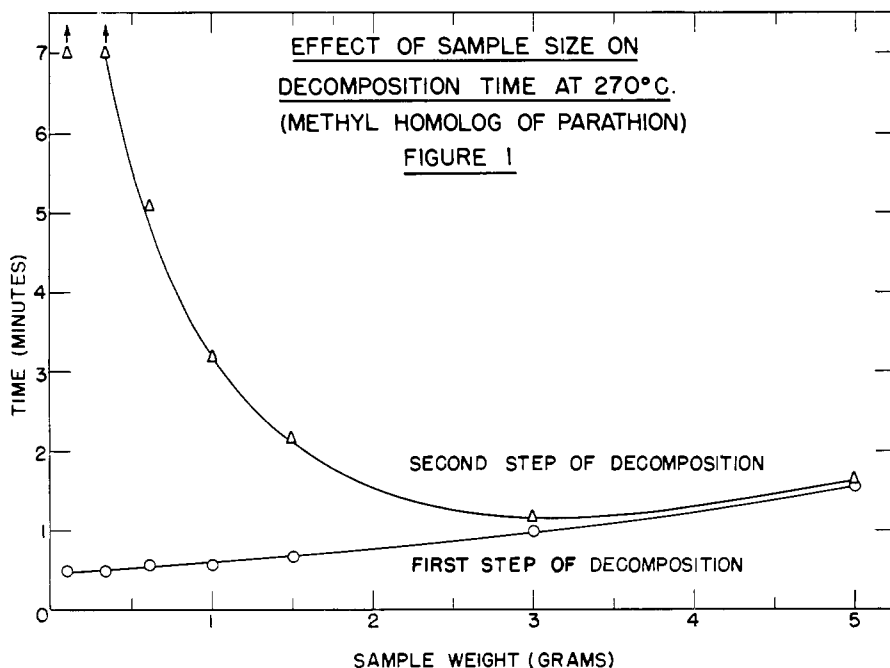
Two samples of *O*-(2-chloro-4-nitrophenyl) *O,O*-dimethyl phosphorothioate (Insecticide 4124) were used. Both

were white crystalline solids. That used for the high temperature decomposition studies melted at 50.5–51.5° C. (corr.). That used for the low temperature studies melted at 50.3–50.8° C. (corr.). Analysis. Calculated for C₈H₈ClNO₅PS: nitrogen, 4.71; sulfur, 10.8. Found: nitrogen, 4.92; thiono sulfur, 10.9; total sulfur, 10.9.

A technical grade sample of *O*-(3-chloro-4-nitrophenyl) *O,O*-dimethyl phosphorothioate (Chlorothion, manufactured by Farben Fabriken Bayer), indicated to be 90% pure, was used.

Experimental and Discussion

The course of the thermal decomposition of phosphorothioates can best be observed by heating the methyl homolog of parathion to temperatures above 200° C. When a 0.5- to 1.5-gram sample



of the pure compound in a small test tube (8 × 73 mm.) was immersed in a Wood's metal bath at 270° C., it immediately melted to a clear liquid which underwent no visible change for approximately 54 seconds. At the end of that time, however, a relatively sudden effervescence occurred which subsided within about 5 to 10 seconds, during which heat was generated and a gas with a strong mercaptan-like odor was evolved. A dark liquid remained which was viscous even at the elevated temperature. This reaction is referred to as the first step of decomposition. When the viscous residue was heated for approximately 5 minutes more, a sudden dephlagration occurred, causing the evolution of copious black fumes and leaving a spongy carbonaceous residue. This is termed the second step of decomposition. It presumably results in complete destruction of the organic molecules present and probably involves the aromatic nitro group.

A similar pattern of decomposition was observed for parathion, Insecticide 4124, and Chlorothion, although the decomposition time at a given temperature varied with the compound tested. The first decomposition step was observed also for malathion. The second step, however, did not occur, possibly because malathion does not contain a nitrophenyl group.

Because of the exothermic nature of the first decomposition step, an increase in sample size to 5 grams or more of the parathion-type compounds caused the first and second decomposition steps to occur practically simultaneously and in some cases with flame formation. The data in Figure 1 were obtained using the technical grade methyl homolog of parathion.

Analyses of Decomposition Products

A small sample (1.6 grams, sample A) of pure *O,O*-dimethyl *O*-(*p*-nitrophenyl) phosphorothioate was heated at 273° C. until the first decomposition step had occurred. The evolved gases were collected in a gas cell by simple air displacement. Infrared analysis showed the products to be dimethyl sulfide and sulfur dioxide.

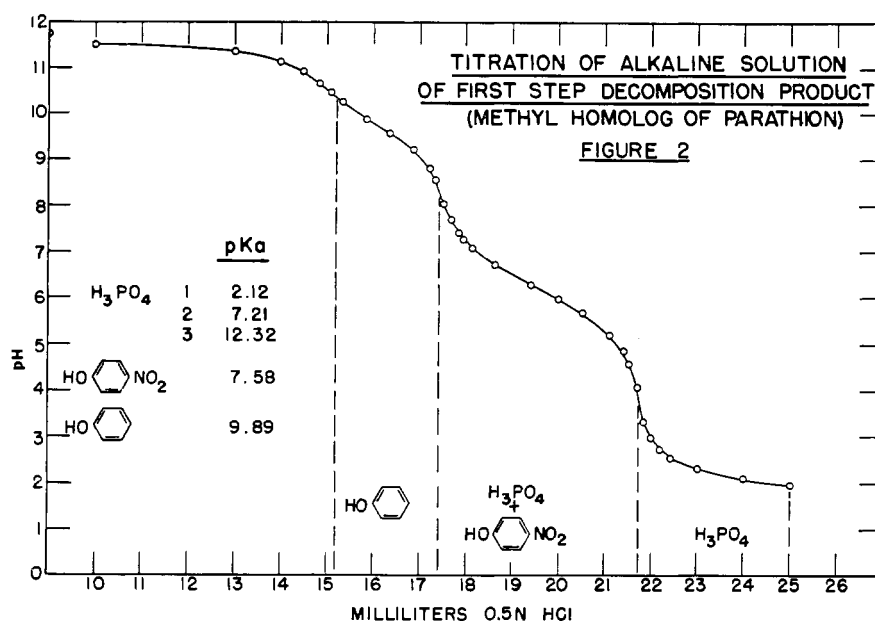
Five determinations of weight loss of the methyl homolog of parathion during the first step of decomposition gave values ranging from 16.25 to 26.0%, the average loss in weight being 22.95%.

A 1-gram sample of the methyl homolog of parathion (sample B) was heated at 268° C. for about 1 minute beyond the occurrence of the first decomposition step. The brown, hygroscopic, very viscous liquid, which was insoluble in ether or benzene, mostly soluble in acetone, and slowly soluble in aqueous alkali, had the following analyses: carbon, 35.75, 35.74; hydrogen, 3.20, 3.24; phosphorus, 13.40, 13.34. The average molecular weight (ebullioscopic method) was found to be 684. Nitrogen was not determined, as nitrogen loss was not anticipated.

The decomposition residue is undoubtedly a mixture of compounds. The average molecular weight of this mixture and the ease with which it dissolved in aqueous alkali suggested the presence of a polymer of relatively low molecular weight, probably a poly(*p*-nitrophenyl metaphosphate). Alkaline hydrolysis of the polymetaphosphate would be expected to give equimolar quantities of phosphate ion and *p*-nitrophenoxide ion. Consequently, this hypothesis was tested by titrating an alkaline solution of decomposition residue with hydrochloric acid.

A sample of the pure methyl homolog of parathion (0.6835 gram, sample C) was heated at 270° C. until the rapid effervescence, indicating first step of decomposition, had occurred. The remaining viscous residue, weighing 0.5317 gram, was dissolved in 25 ml. of 0.5*N* aqueous sodium hydroxide and allowed to stand overnight. Titration of the alkaline solution with 0.5*N* hydrochloric acid gave the curve shown in Figure 2.

Interpretation of the titration curve was consistent with the presence of 1.63 millimoles of phosphate ion, 0.53 millimole of *p*-nitrophenoxide ion, and 1.13 millimoles of an acid (p*K*_a 9.5 to 10.0) weaker than *p*-nitrophenol (p*K*_a 7.58). Assuming the weaker acid to be a phenol, a total of 1.66 millimoles of phenolic compound was indicated—that is to say, hydrolysis of the viscous decomposition residue yielded equimolar quantities of phosphate ion and of mixed phenols (approximately 30 mole % being *p*-nitrophenol). Phenol itself, having a p*K*_a of 9.89, is the most likely possibility for the weak acid.

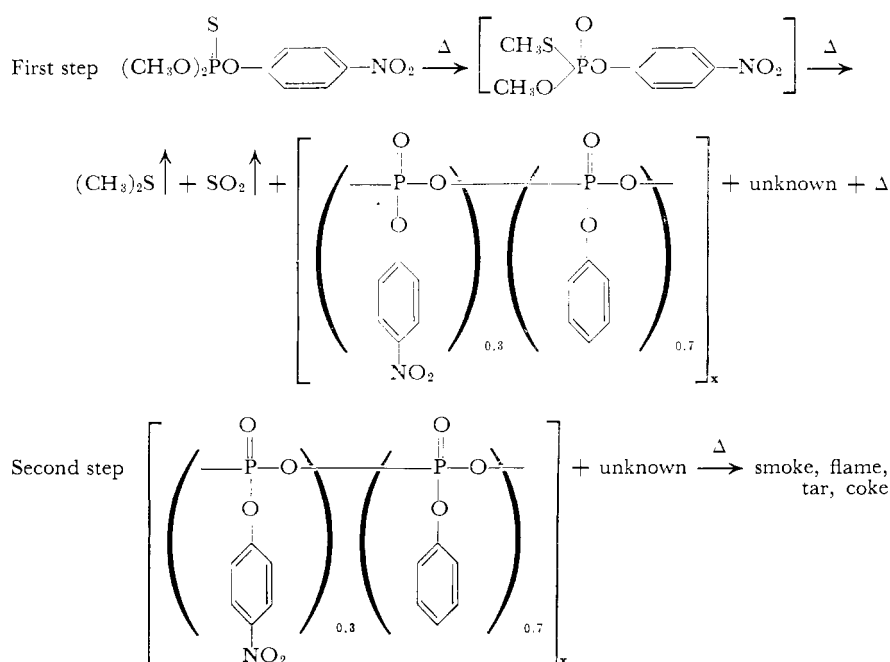


A mixture of 1.65 millimoles of phosphoric acid, 0.5 millimole of *p*-nitrophenol, and 1.15 millimoles of phenol was then dissolved in 25 ml. of 0.5*N* sodium hydroxide and was titrated with 0.5*N* hydrochloric acid as before. The resulting titration curve (Figure 3) indicated the presence of 1.63 millimoles of phosphate ion, 0.65 millimole of *p*-nitrophenoxide ion, and 1.15 millimoles of phenoxide ion. This curve was practically identical with the titration curve obtained from the thermal decomposition residue.

It is felt, therefore, that the viscous residue contains a mixed poly metaphosphate or mixture of polymetaphosphates (approximately 70% phenyl and 30% *p*-nitrophenyl). Thus the first step of decomposition and the subsequent total decomposition of the viscous residue may be represented by the following:

The formation of sulfur dioxide and the loss of nitro groups during the course of thermal decomposition would not be unexpected, considering the known reducing nature of thiono sulfur and the oxidizing nature of aryl nitro groups. In another section of this laboratory, sulfur treatment of *o*-nitrotoluene at 250° C. led to the formation of sulfur dioxide and a black, tarry residue (12). Moreover, the reduction of nitro compounds to amines by sodium sulfide, which in the process was oxidized to sodium thiosulfate, has been reported by Goldschmidt and Larsen (5).

The decomposition residue is undoubtedly a mixture of compounds and the formula suggested above therefore represents only part of what occurs. The phosphate ion found by titration, for instance, was only about 62% of the amount theoretically possible from the



methyl homolog of parathion. Moreover, assuming the presence of the polymetaphosphate to be correct, the titratable portion—polymetaphosphate—of the decomposition residue represented only about 50% of the sample weight. The theoretical weight change for the above reaction due to the loss of dimethyl sulfide is 35.8%, whereas approximately 23% loss was observed. The theoretical analyses for the proposed polymetaphosphate compare with the observed values (from sample B) as follows:

	Theory	Found
C	43.23	35.74
H	2.88	3.22
P	18.59	13.37

Assuming that approximately the same analytical results would be obtained from any sample of the first-step decomposition residue, these data in combination with the titration data (obtained from sample C) allow one to conjecture concerning the ratio of carbon, hydrogen, and phosphorus in that portion of the decomposition mixture which was not titratable.

In sample C of the residue (weighing 0.5317 gram), 0.2705 gram of the polymetaphosphate was detected by titration. This titrated portion should theoretically contain 0.117 gram of carbon, 0.0078 gram of hydrogen, and 0.0503 gram of phosphorus. The amounts of these elements actually present in the entire 0.5317 gram of sample C, according to the analytical results obtained from sample B, are 0.19 gram of carbon, 0.0171 gram of hydrogen, and 0.071 gram of phosphorus. There should be therefore, in the 0.2612 gram of sample C which did not titrate, 0.073 gram of carbon (28%), 0.0093 gram of hydrogen (3.56%), and 0.0207 gram of phosphorus (7.92%). Thus the carbon-hydrogen-phosphorus ratio in the untitrated portion of the sample should approximate 9:14:1.

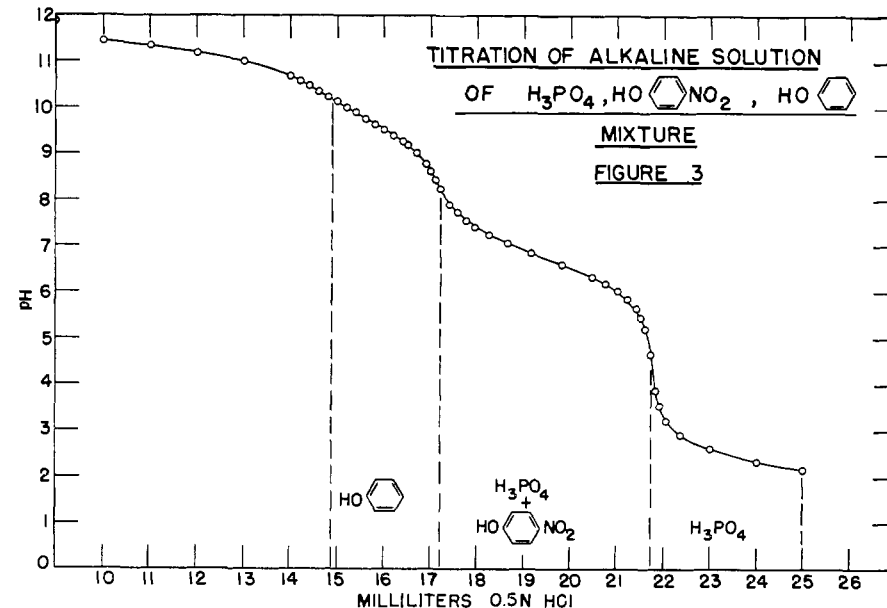
A very small quantity of tan, crystalline solid, melting at 157–160° C., was separated from the solution of decomposition residue after titration. Another small sample of solid, melting at 152–154° C., was obtained by dissolving the viscous decomposition residue in acetone and treating with an equal volume of water. However, the identity of neither the crystalline solids nor the remaining untitrated portion of the residue has been determined.

Determination of Decomposition Times

High Temperature Studies

In this investigation it was of particular interest to determine the time for decomposition to occur at various temperatures for some of the phosphorothioate insecticides, so that the "stable lives" of these com-

pounds would be known at temperatures that might be encountered during the course of their preparation.



pounds would be known at temperatures that might be encountered during the course of their preparation.

As it had been found that at 270° C. no time interval existed for the methyl homolog of parathion between the first step of decomposition and the second total decomposition step for samples larger than 3 to 5 grams (Figure 1), it was apparent that measurement of the time to the first step of decomposition at a given temperature for small samples would give in effect the expected time of total decomposition for large amounts of material.

The sudden effervescence which occurred during the first decomposition step was visible and its time of occurrence could readily be measured. Thus decomposition times were determined by immersing 0.2-gram samples of insecticide in 8 × 73 mm. test tubes in a Wood's metal bath at a given temperature and noting the time to effervescence. In this study, therefore, the term "decomposition time" refers to an empirical measurement—the time that a sample may be heated at a given temperature until the first step of decomposition occurs. No indication of the rate of decomposition, once started, is to be inferred in the term. In all probability it actually represents an over-all induction period leading to the first step of decomposition.

The reproducibility of this measurement is indicated by the decomposition times (Table I) determined for *O*-(2-

chloro-4-nitrophenyl) *O,O*-dimethyl phosphorothioate (Insecticide 4124) at various temperatures.

The observed decomposition times for the five compounds studied are shown in Figure 4.

Using the same data, a straight line may be obtained by plotting $\log 1/t$ against $1/T$, where t is the decomposition time in seconds and T is the absolute temperature. This plot is based on the Arrhenius equation relating reaction rate with temperature.

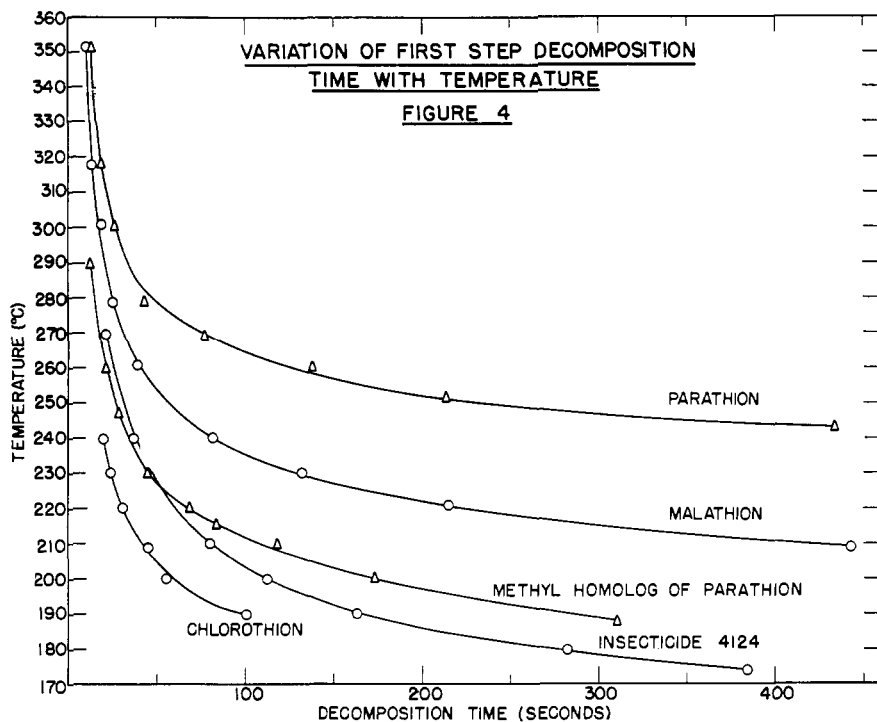
$$\log k = -\frac{E}{2.303 \times R} \times \frac{1}{T} + C$$

According to this equation, a straight line results when the logarithm of the specific reaction rate is plotted against the reciprocal of the absolute temperature. Although the specific reaction rate has not been determined in these studies, the authors have measured, at several different temperatures, the time required for the first-step decomposition to reach what is assumed to be the same extent of reaction. The reciprocal of the decomposition time is proportional to the reaction rate. Consequently, its log should also give a straight line when plotted against $1/T$. A correction must be applied, however, to account for the time required for the sample to reach bath temperature.

Application of this correction is demonstrated, using the data for the methyl

Table I. First-Step Decomposition Time of Insecticide 4124

	Temperature, ° C.						
	270	240	210	200	190	180	174
	Decomposition Time, Seconds						
	21.5	37	86	115	169	272	389
	21.5	36	77	109	157	292	379
	21.6	..	76	113
Average	21.5	36.5	80	112	163	282	384



homolog of parathion, in Figure 5. The initial plot gives a straight line in the lower temperature region, but curves in the higher temperature region. By extrapolating the straight line toward the higher temperatures, an average difference of 9 seconds between the measured

and extrapolated values was obtained for the methyl homolog. A straight line was obtained over the entire region by applying the 9-second correction to all the observed decomposition times. As the time correction is negligible in the lower temperature region, there is no

change in slope between the corrected plot and the original straight-line plot. By replotting the original data in a similar manner for all the compounds tested, a family of straight lines was obtained (Figure 6).

In this plot the portion enclosed by dotted lines represents the decomposition times observed experimentally. By extrapolation it is possible to estimate when decomposition might be expected to occur at much lower temperatures. Examples of the extrapolated values are given in Table II.

Low Temperature Studies

As a test of the accuracy of these extrapolated values, samples of Insecticide 4124 were heated at 65°, 80°, and 115° C. for varying lengths of time and studied for evidence of decomposition. At these temperatures the decomposition, once started, occurs at a much slower rate. And because of the necessarily small sample size (1 gram), the heat of reaction readily dissipates. Thus the effervescence which is easily observed with decomposition in the 175° to 350° C. range is not evident at the lower temperatures. For this reason reduction in percentage of thiono sulfur with time, as determined by a modification of the method of Schrader (2) was instead observed.

At 180° C. decreasing thiono sulfur content with time was measured and

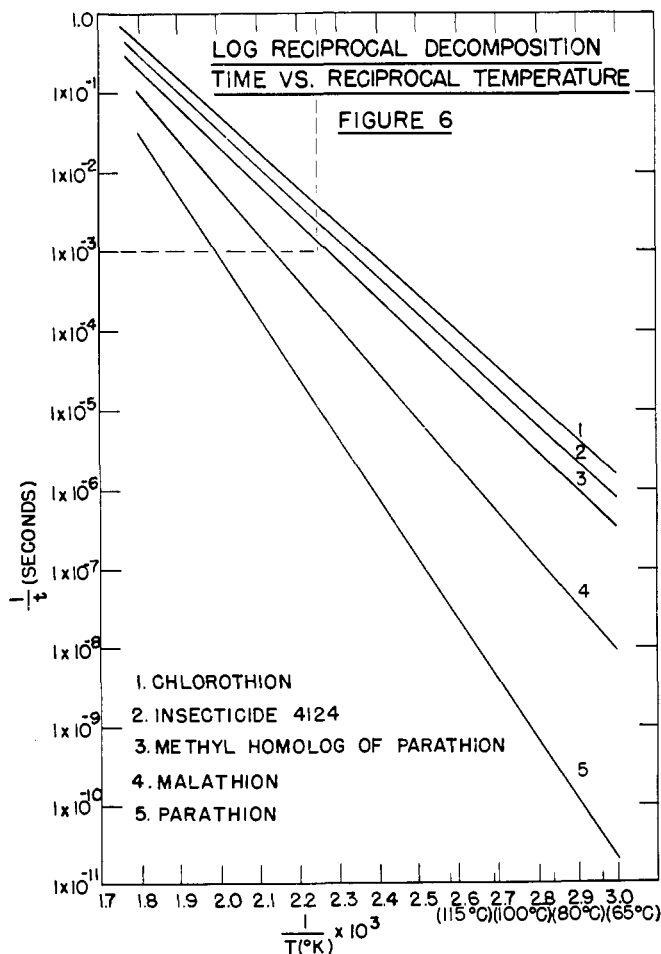
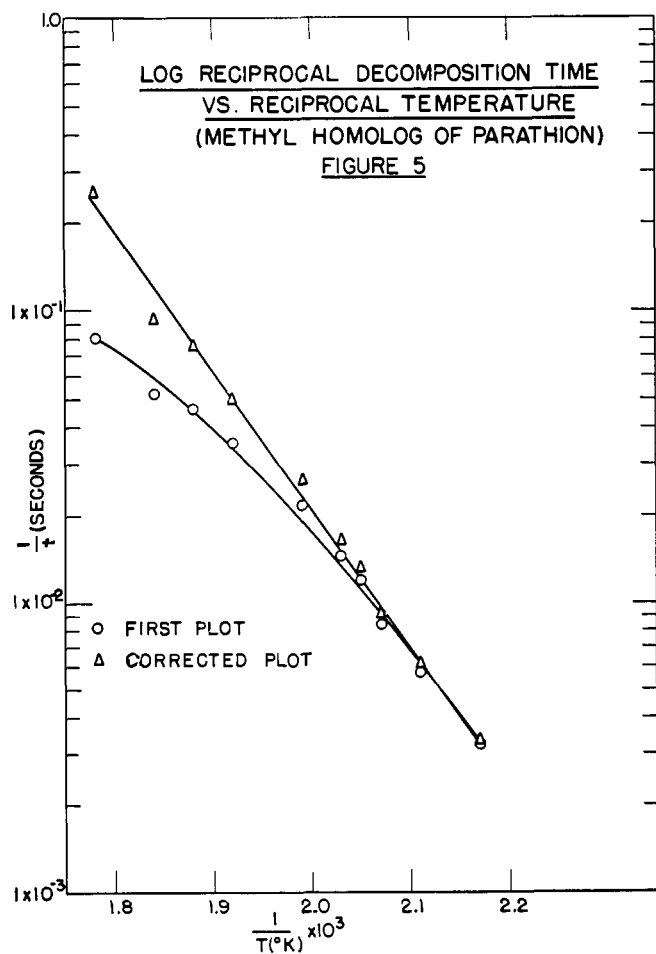


Table II. Estimated Decomposition Time

Temp., ° C.	Decomposition Time, Days				
	Parathion	Malathion	Methyl homolog of parathion	Insecticide 4124	Chlorothion
115	340	5	7.9 hours	3.9 hours	2.2 hours
100	2200	20	26 hours	11.9 hours	6.7 hours
80	...	163	5.6	2.5	32 hours
65	...	925	23	9.6	5

compared directly with an observable decomposition (Figure 7).

Similar comparisons of thiono sulfur content with time at 115°, 80°, and 65° C. are shown in Figures 8 and 9. In these cases, although visible evidence of decomposition could not be obtained, the estimated time of expected decomposition obtained by extrapolation is shown by the dotted lines.

It is evident that reduction in thiono sulfur content commenced at approximately the estimated decomposition time. This probably marked the beginning of the conversion of Insecticide 4124 to its *S*-methyl isomer. However, some decomposition seemed to be occurring simultaneously, as a faint but unmistakable odor of dimethyl sulfide was noticed in nearly all the samples subjected to the low temperature storage tests.

It is possible, therefore, that for phosphorothioates of the parathion type, and particularly the methyl homologs, decomposition may occur shortly after or even simultaneously with isomerization. As thermal decomposition of parathion itself at elevated temperatures has also been demonstrated, the possibility of concurrent isomerization and decomposition for parathion and higher homologs should not be overlooked. It is admitted, however, that isomerization of parathion, as indicated by reduction in thiono sulfur content, has been reported repeatedly in the literature at 150° C. within times (up to 24 hours) much shorter than would be estimated by extrapolation from these studies (approximately 7 days at 150° C.). Nevertheless varying degrees of decomposition may have occurred in the previous cases described in the literature, as reduction in thiono sulfur content will be observed either for decomposition or for isomerization, and thus will not distinguish between the two.

Early determinations of thiono sulfur in this laboratory gave unusually high results, which had been observed in a few cases in the literature. Woodcock and Stringer (15) suggested that coprecipitation of barium nitrate with barium sulfate caused the high values. Members of the analytical staff in this laboratory confirmed this explanation and developed the following procedure based on that of Schrader (2).

Determination of Thiono Sulfur in Parathion or Its Homologs. A.

PRINCIPLE. The thiono sulfur in compounds containing the $\text{ROP}-\overset{\text{S}}{\parallel}$ group is oxidized to sulfate when refluxed with 12*N* nitric acid. The isomer $\text{RS}-\overset{\text{O}}{\parallel}{\text{P}}$ will not oxidize under these conditions. Thus, thiono sulfur may be calculated from the amount of sulfate determined

and provides another convenient measure of the purity or degree of isomerization of the insecticide. The sulfate formed from the thiono sulfur is precipitated from a large volume to avoid high results due to nitrate coprecipitation.

B. REAGENTS. Nitric acid, 12*N*. Dilute 79 ml. of concentrated nitric acid, specific gravity 1.42, to 100 ml. with water.

Ammonium hydroxide, 7*N*. Add 50 ml. of reagent grade ammonium hydroxide to 50 ml. of water.

Hydrochloric acid, concentrated, reagent grade.

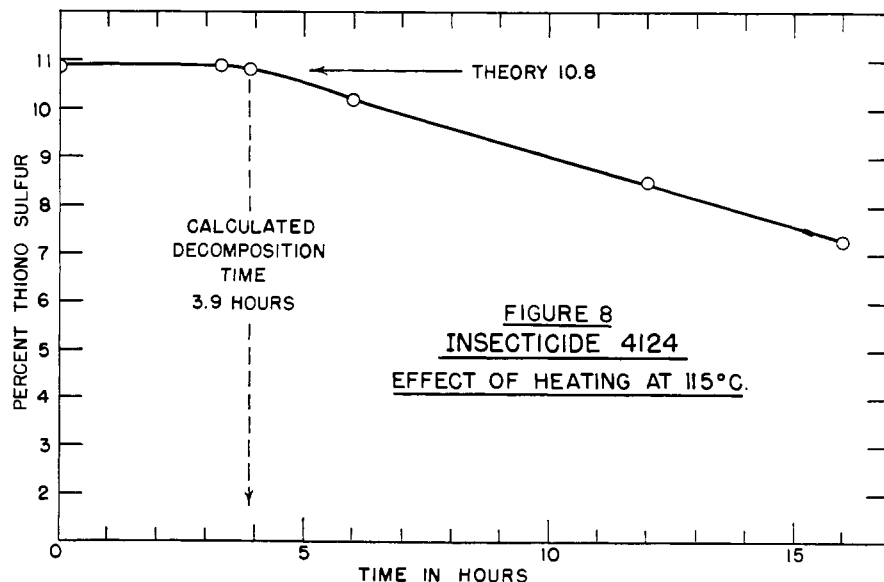
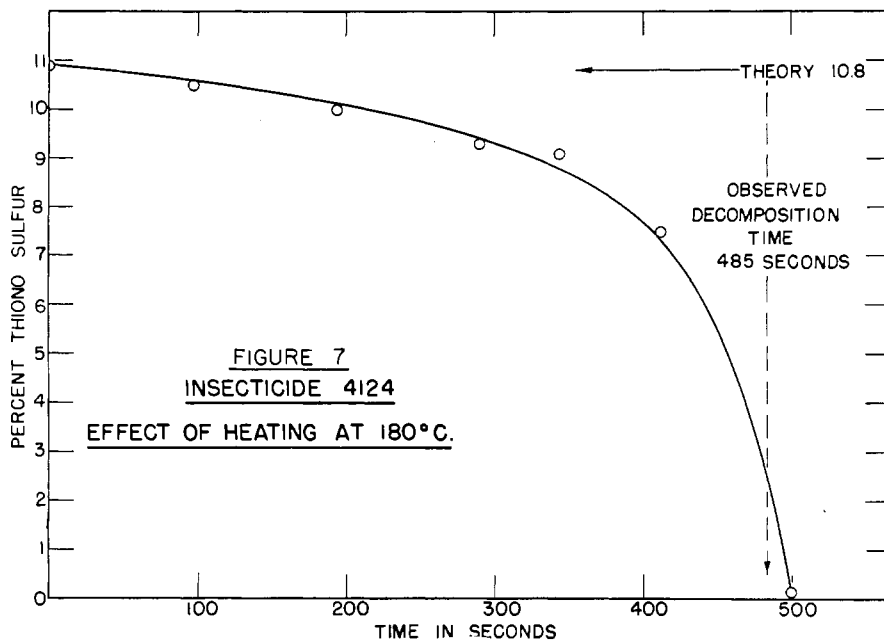
Barium chloride, reagent grade, 10% aqueous solution.

Hydrochloric acid wash solution. Add 1 ml. of concentrated hydrochloric acid to 100 ml. of water.

C. APPARATUS. Erlenmeyer flasks, 250-ml., with ground-glass joints.

Air condensers to fit flasks

Beakers, 1000-ml. Griffin low-form



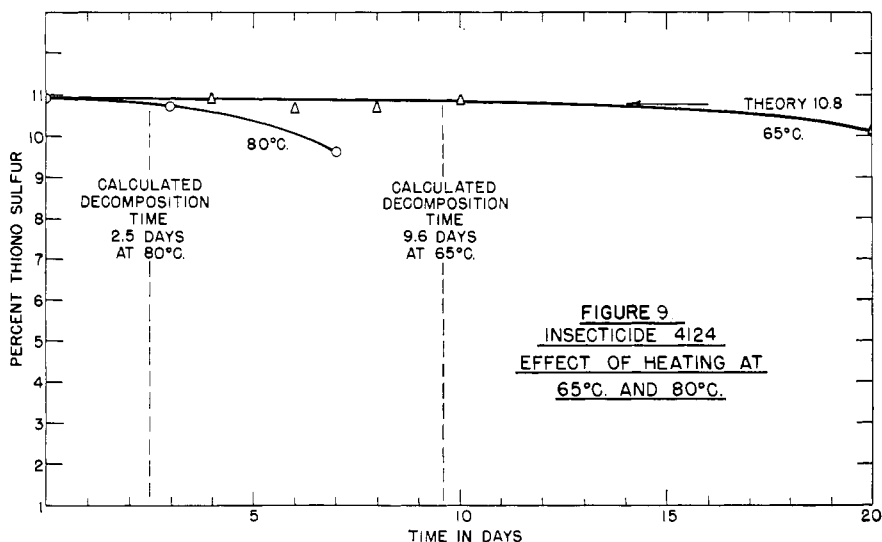


FIGURE 9
INSECTICIDE 4124
EFFECT OF HEATING AT
65°C. AND 80°C.

Platinum crucibles
Infrared drying lamps
Muffle furnace

D. PROCEDURE. Weigh accurately 0.4 gram of sample and transfer to a 250-ml. Erlenmeyer flask. Add 15 ml. of 12*N* nitric acid, attach an air condenser, and reflux gently on a steam bath for 3 hours. Cool, and transfer the solution quantitatively to a 1-liter beaker with the aid of water from a wash bottle. Dilute to approximately 400 ml. and make alkaline by cautiously adding approximately 25 ml. of 7*N* ammonium hydroxide, stirring continuously during the addition. Reacidify by adding concentrated hydrochloric acid in 1-ml. portions, testing with indicator paper between additions. Add 3 ml. of concentrated hydrochloric acid in excess and dilute with water to 800 ml. Heat to boiling and precipitate the sulfate by dropwise addition of 10 ml. of 10% barium chloride, stirring constantly during the precipitation. Digest the precipitate on a steam bath for 3 hours, or allow to stand overnight. Filter on No. 42 Whatman paper containing a small amount of paper pulp. Wash three times with cold hydrochloric acid wash solution. Finally, wash

several times with warm water until a test for chloride is negative. Transfer to a platinum crucible which has been previously ignited at 800° C. and accurately tared. Dry and char the paper under infrared heat, then place the crucible in a muffle furnace. Ignite at 800° C. for 1 hour, remove from the furnace, cool in a desiccator, and weigh.

E. CALCULATION

$$\frac{\text{Grams of BaSO}_4 \times 13.74}{\text{grams of sample}} = \% \text{ thiono sulfur}$$

Effect of Catalysts on Phosphorothioate Decomposition

Although the thermal decomposition of phosphorothioates is readily observed when pure compounds are used, the onset of decomposition can be hastened in the presence of catalysts. Salts of iron and copper were found to catalyze the decomposition of the methyl homolog of parathion. Other metallic salts might be expected to show a similar effect. No catalytic action was apparent at 190° C., however, for powdered iron, concentrated phos-

phoric acid, or concentrated hydrochloric acid.

Table III. Decomposition Time of Methyl Homolog of Parathion at 190° C. in Presence of Catalysts

Catalyst (5% Concn.)	First-Step Decomposition Time, Seconds
None	244, 227, 246
FeCl ₃ ·6H ₂ O	100
FeCl ₂ ·4H ₂ O	70 (approx.)
Cu ₂ Cl ₂	92
CuCl ₂ ·2H ₂ O	91
CuCl ₂	73

phoric acid, or concentrated hydrochloric acid.

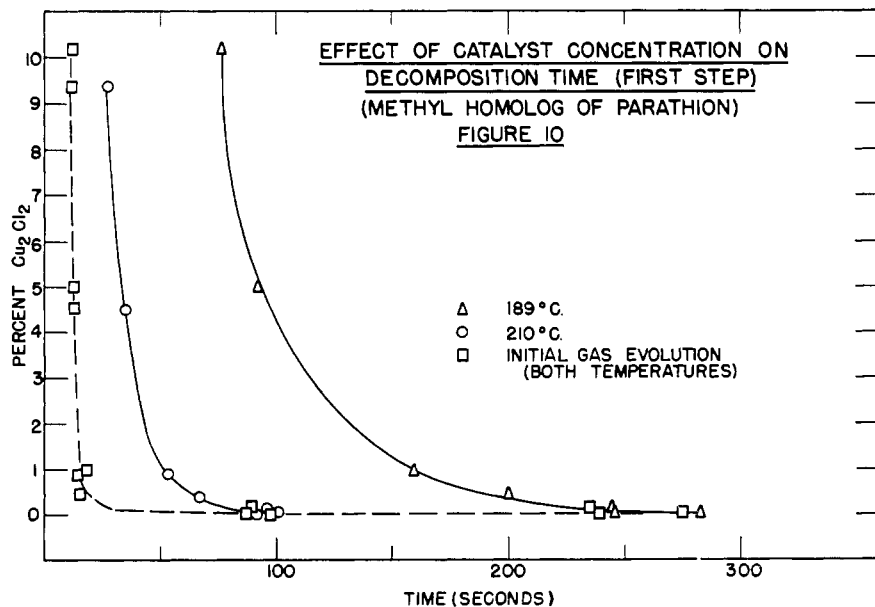
The effect of catalyst concentration, using cuprous chloride as an example, on the decomposition of methyl homolog of parathion is seen in Figure 10. The solid lines represent normal first phase decomposition at two different temperatures. The dotted line indicates brief evolution of a small amount of gas which occurred shortly after the sample reached bath temperature, and only in the presence of catalyst. The cause of this initial gas evolution is not known, although it is thought to be due to the release of gas or moisture adsorbed by the catalyst.

Summary and Conclusions

It is apparent that prolonged heating of the methyl homolog of parathion and similar phosphorothioates can lead to changes more extensive than mere conversion to the *S*-alkyl isomer. Although isomerization probably occurs first, it is followed by a two-step decomposition.

The first step, an exothermic reaction which can be hastened by catalysts such as metallic salts, evolves dimethyl sulfide (in the case of the methyl homolog of parathion) and sulfur dioxide. It leaves a polymeric residue which is slowly soluble in aqueous alkali, but insoluble in organic solvents such as benzene or ether. The presence of a mixed phenyl and *p*-nitrophenyl polymetaphosphate is indicated in the residue by titration analysis. This polymetaphosphate mixture on further heating undergoes a second step of decomposition, at times explosively, leaving a carbonaceous residue.

The possibility that eventual decomposition may occur, after varying times depending upon the temperature, should be borne in mind for phosphorothioates even at temperatures frequently used for their preparation—e.g., 65° to 115° C. The effects of this decomposition may be felt simply as degradation of product quality. It is possible, however, especially at somewhat higher temperatures, and under conditions where the heat of reaction of the first decomposition step cannot be adequately removed, that explosive decomposition may occur. A rough approximation of the theoretically possible decomposition times at temperatures of 65° C. and



EFFECT OF CATALYST CONCENTRATION ON DECOMPOSITION TIME (FIRST STEP) (METHYL HOMOLOG OF PARATHION) FIGURE 10

△ 189° C.
○ 210° C.
□ INITIAL GAS EVOLUTION (BOTH TEMPERATURES)

higher may be obtained by referring to Figure 6 and Table II. This gives only an estimate, however, and should not be relied upon alone. It is recommended, therefore, that the maintenance of thiono sulfur content, observed for small samples, should serve as the criterion for determining whether heat treatment of phosphorothioates at a given temperature and for a given time is apt to lead to decomposition.

The use of a continuous distillation process for removal of solvent from phosphorothioate insecticides allows short contact time at the distillation temperature and reduces the possibility of product decomposition to a minimum.

The decomposition described here may have been a factor bearing on the varying results which have been obtained in the past in comparing either the insect or mammalian toxicity of parathion or its homologs with their *S*-alkyl isomers, particularly in cases where the isomers were prepared by heat treatment of the parent insecticides. The absence of contact insecticidal activity, for instance, reported by Martin (7) for the methyl homolog of parathion after heating for 6 hours at 150° C. to nearly zero thiono sulfur content may have been due to the presence of mixed polymeta-

phosphates. It is estimated from the present studies that decomposition of the methyl homolog could occur in approximately 40 minutes at 150° C. Although the polymetaphosphates should be effective phosphorylating agents and thus should show in vitro inhibition of cholinesterase, their lack of solubility in benzene or ether should indicate low permeability to the insect cuticle and thus low contact insecticidal activity.

Acknowledgment

The authors are indebted to D. J. Salley and J. J. Carnes for their helpful suggestions, to G. A. Clarke, William Hart, and M. V. Norris for development of the modified thiono sulfur determination, to E. F. Williams for determination of the purity of materials by the cryoscopic method, and to members of the analytical staff for molecular weight, infrared, and other determinations.

Literature Cited

- (1) Bright, N. F. H., Cuthill, J. C., and Woodbury, N. H., *J. Sci. Food Agr.* **1**, 344 (1950).
- (2) Coates, H., and Topley, B., *PB 95*, 312 (BIOS 1808), "Synthetic Insecticides," interrogation of Gerhard Schrader, 1947,

Technical Information and Document Unit, 40 Cadogan Square, London, S. W. 1.

- (3) Diggle, W. M., and Gage, J. C., *Biochem. J.* **49**, 491 (1951).
- (4) Emmett, W. G., and Jones, H. O., *J. Chem. Soc.* **99**, 713 (1911).
- (5) Goldschmidt, H., and Larsen, H., *Z. phys. Chem.* **71**, 437 (1910).
- (6) Jura, W. H., *Anal. Chem.* **27**, 525 (1955).
- (7) Martin, H., *J. Sci. Food Agr.* **1**, 163 (1950).
- (8) Metcalf, R. L., and March, R. B., *J. Econ. Entomol.* **46**, 288 (1953).
- (9) Morrill, H. L. (to Monsanto Chemical Co.), U. S. Patent **2,601,219** (June 17, 1952).
- (10) Norris, M. V., Stamford Laboratories, American Cyanamid Co., private communication.
- (11) O'Keefe, K., and Averell, P. R., *Anal. Chem.* **23**, 1167 (1951).
- (12) Sutherland, G. L., Stamford Laboratories, American Cyanamid Co., private communication.
- (13) Topley, B., *Chemistry and Industry 1950*, S859.
- (14) Witschonke, C. R., *Anal. Chem.* **24**, 350 (1952).
- (15) Woodcock, D., and Stringer, A., *Ann. Appl. Biol.* **38**, 111 (1951).

Received for review April 16, 1955. Accepted July 18, 1955. Division of Agricultural and Food Chemistry, Pesticides Subdivision, 127th Meeting, ACS, Cincinnati, Ohio, March 1955.

INSECTICIDE SYNERGISTS

3,4-Methylenedioxyphenoxy Compounds as Synergists for Natural and Synthetic Pyrethrins

MORTON BEROZA

Entomology Research Branch,
Agricultural Research Service,
U. S. Department of Agriculture,
Beltsville, Md.

The discovery that a compound containing the 3,4-methylenedioxyphenoxy group produces a greater degree of synergism with pyrethrins than the corresponding compound containing a 3,4-methylenedioxyphenyl group, as in sesamolin and sesamin, led the author to synthesize new compounds containing the methylenedioxyphenoxy group as candidate synergists. This paper describes the preparation and properties of 66 of these compounds. In preliminary tests with the housefly by the turntable method, almost all the ethers, acetals, and sulfonates showed synergism, the urethans showed lesser activity, whereas the esters of carboxylic acids showed practically no synergism. Some of the compounds were sufficiently active to merit further study.

SOME OF THE BEST AND SAFEST INSECTICIDAL MATERIALS have been developed from the study of naturally occurring products. Synergists for pyrethrum fall in this category. From sesame oil Haller, LaForge and Sullivan (6) isolated sesamin, a compound found to be strongly synergistic with pyrethrins. By examination of compounds similar to sesamin, the 3,4-methylenedioxyphenyl

group was shown to be necessary for sesamin's activity.

The fundamental work of Haller and his associates triggered the search for synthetic synergists that could be prepared cheaply enough to be of commercial value. The search has led to the production of such excellent pyrethrum synergists as piperonyl butoxide (14), sulfoxide (13), piperonyl cyclonene (14),

and *n*-propyl isome (12), all of which contain the 3,4-methylenedioxyphenyl group.

Of late the synergist problem has been complicated by the introduction of synthetic pyrethrin-like compounds, such as allethrin, introduced by Schechter, Green, and LaForge (17). With this compound and others such as furethrin (9), synergists were found to be much