

the isolation procedures (Stewart and Wheaton, 1967; Orazkuliev et al., 1962; Housholder and Camp, 1965). It has also been claimed to be a plant natural product (Rimington and Roets, 1937). However, triacetoneamine could not be isolated when different methods of extraction were used in this latter case.

The present communication shows that this artifact is produced by reaction of acetone with endogenous components of biological materials.

Due to the natural occurrence of ammonium salts and other reactive amines in fungal material we suggest the use of solvents which do not contain carbonyl functionality in order to minimize artifact production during extraction.

LITERATURE CITED

- Heintz, W., *Annalen* 178, 320 (1875).
Housholder, D. E., Camp, B. J., *J. Pharm. Sci.* 54, 1676 (1965).

- Lodder, J., Kreger-Van Rij, N. J. W., "The Yeasts—A Taxonomic Study", North-Holland Publishing Co., Amsterdam, 1952, pp 12–13.
Orazkuliev, I. K., Otroschenko, O. S., Sadykov, A. S., *Zh. Obshch. Khim.* 32, 3827 (1962).
Rimington, C., Roets, G. C. S., *Onderstepoort J. Vet. Sci. Anim. Ind.* 9, 193 (1937).
Stewart, I., Wheaton, T. A., *Phytochemistry* 6, 1587 (1967).

Leonard F. Bjeldanes*
George W. Chang

Department of Nutritional Sciences
University of California
Berkeley, California 94720

Received for review March 10, 1975. Accepted July 7, 1975.

Identification of the Major Thermal Degradation Products of the Insecticide Mirex

The thermal decomposition of mirex has been studied at temperatures up to 700°. Infrared, mass spectral, gas chromatographic, and ultraviolet data were used to establish that hexachlorobenzene was the major thermal degradation product.

Hexachlorocyclopentadiene was also found in small amounts in the thermal residue. The products identified from the vapor phase were carbon monoxide, carbon dioxide, hydrogen chloride, chlorine, carbon tetrachloride, and phosgene.

Mirex (dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[*cd*]pentalene) has commonly been used in the southern United States to control the imported fire ant. Alley (1973) has reviewed the uses of mirex and the problems caused by its use. This persistent chlorocarbon has been shown to be inert to many common acids, bases, and oxidizing and reducing agents (McBee et al., 1956). Mirex does, however, react with lithium and *tert*-butyl alcohol to give the corresponding hydrocarbon and *endo*-dicyclopentadiene (Dilling et al., 1967). The chlorocarbon also undergoes photolysis in hydrocarbon solvents to yield the monohydro and dihydro derivatives (Alley et al., 1973, 1974).

McBee et al. (1956) and Eaton et al. (1960) have indicated mirex to be thermally stable, pyrolysis occurring only at temperatures above 500°. The thermal degradation products reported in each case are somewhat conflicting. McBee indicated the products to be largely carbonaceous material and chlorine with a trace of hexachlorocyclopentadiene. Eaton, however, reported no carbonaceous material and only trace amounts of hexachlorocyclopentadiene at 500°. The purpose of the present investigation was to investigate the thermal degradation products of mirex in relationship to disposal of this insecticide by incineration.

EXPERIMENTAL SECTION

Analytical standard grade, 99.9% mirex, donated by Allied Chemical Corporation, was used without further purification. Hexachlorocyclopentadiene was obtained from Aldrich Chemical Co. Reagent grade hexachlorobenzene (Eastman Chemical Co.) was further purified by recrystallization. The thermal lability of mirex was circumvented by sealing 50–100-mg samples in 10-ml Neutraglas ampules. The samples were heated in a muffle furnace for 30 min at the selected temperatures, removed and allowed to cool, and broken, and the contents dissolved in pesticide grade hexane.

Identification of Hexachlorobenzene. The major com-

ponent of pyrolysis of mirex was identified by the retention times on four columns of differing polarities with McReynolds constants for benzene ranging from 15 to 321. Specifically, gas-liquid chromatographic identification was accomplished by use of a Barber-Colman 5000 series gas chromatograph equipped with a tritium foil electron capture detector and a Varian Aerograph Model 1400 gas chromatograph equipped with a flame ionization detector. Both columns used in the Barber-Colman chromatograph were 1.8 m × 4 mm i.d. glass and were packed with 3% OV-1 on Chromosorb W 80–100 mesh and 1.5% OV-17, 1.95% QF-1 on Chromosorb W 100–120 mesh. Chromatographic conditions for both columns were as follows: injector, column, and detector temperatures of 225, 110, and 215°, respectively. Carrier gas was nitrogen at a flow rate of 100 ml/min. Two columns were also used in the Varian Aerograph chromatograph. The 5% SE-30 on Anakrom ABS 80–90 mesh (1.2 m × 2 mm i.d.) was operated with injector, column, and detector temperatures of 175, 150, and 180°, respectively. The 5% Carbowax 20M on Anakrom ABS 60–80 mesh (2.4 m × 2 mm i.d.) was operated with injector, column, and detector temperatures of 200, 120, and 210°, respectively. Nitrogen was used as a carrier gas in both instances. Flow rates were 15 ml/min for both the SE-30 column and the Carbowax 20M column.

Mass spectral analysis was accomplished by use of a Perkin-Elmer Model 270 GC-MS equipped with a 5% SE-30 on Anakrom ABS 60–80 column (2.4 m × 3 mm i.d.) operated at 100° with a nitrogen flow rate of 10 ml/min. The mass spectrum was identical with that of hexachlorobenzene.

Prior to infrared analysis, isolation was accomplished by the passing of the thermal residue through a 19 in. × 1 in. alumina column and elution with cyclohexane. The major component was recrystallized by solvent evaporation and redissolved in carbon disulfide. Analysis was performed on a Perkin-Elmer Model 457 spectrophotometer. The in-

frared spectrum was identical with that of hexachlorobenzene.

Ultraviolet analysis was performed by use of a Beckman ACTA-V spectrophotometer. The thermal residue was dissolved in hexane, with the spectrum obtained being identical with that of hexachlorobenzene.

Identification of Hexachlorocyclopentadiene. Hexachlorocyclopentadiene was identified by its retention time on the 3% OV-1, 1.95% QF-1-1.5% OV-17, and 5% Carbowax 20M columns under the conditions described in the previous section. The columns were operated at 110° to separate the rapidly eluting hexachlorocyclopentadiene from the solvent peak.

Identification of Vapor Phase Products. The identification of the gaseous products of the pyrolysis of mirex contained in the ampules was by mass spectrometry and gas chromatography. A Varian Model EM-6270 gas sampling valve was used for initial identification. Gaseous samples were introduced into the spectrometer at an inlet temperature of 180° and the spectra were obtained at an ionizing voltage of 70 eV. Confirmation was by gas chromatography using a Barber-Colman 5000 series gas chromatograph equipped with a thermal conductivity detector. Columns used were Porapak Q 50-80 mesh, molecular sieve 13X 60-80 mesh, and 10% Arochlor 1232 on Chromosorb T 40-60 mesh. The Porapak Q and 10% Arochlor 1232 columns were 1.8 m × 4 mm i.d. glass and the molecular sieve column was 1.8 m × 5 mm i.d. stainless steel. Injector and column temperatures were ambient temperature and the detector temperature was 110°. Helium at a flow rate of 20 ml/min was used as carrier gas. Since a phosgene standard was not available, this identification was made on the basis of the fragmentation pattern and the parent peaks at 98 and 100 mass units.

These gaseous products are consistent with the predictions of the NASA/LEWIS Chemical Equilibrium Calculations, which were performed to support the experimental data (Gordon and McBride, 1971).

RESULTS AND DISCUSSION

No degradation of the analytical standard grade mirex was detected by either gas-liquid chromatography or infrared spectroscopy below 525°, which is in agreement with previous investigations (McBee et al., 1956; Eaton et al., 1960). The residue remaining after 50-100-mg mirex samples were heated to 525° showed seven peaks on the gas chromatogram obtained with OV-17, QF-1 column. The retention times relative to mirex were 0.004, 0.006, 0.011, 0.045, 0.057, 0.081, and 0.207, respectively. The chromatograms of samples heated to 600° contained only peaks corresponding to the first, third, sixth, and seventh peaks found at 525°. The relative sizes of the peaks were such that the sixth peak was 16 times larger than any other peak. This component has been identified as hexachlorobenzene by gas-liquid chromatography, mass spectroscopy, infrared spectroscopy, and ultraviolet spectroscopy. The third peak ($t_R = 0.011$) was identified as hexachlorocyclopentadiene by gas-liquid chromatography. This component was in very low concentration, especially at the higher temperatures.

A sample of mirex heated to 550° in an ampule was found to lose 15% of its original weight on the average. The residue remaining proved to be 72% by weight hexachlorobenzene. Thus, the hexachlorobenzene yield was about 60% and indicated a 1:1 mole ratio between mirex and hexachlorobenzene. Analysis of the gaseous products indicated these to consist predominantly of carbon monoxide, carbon dioxide, hydrogen chloride, chlorine, and carbon tetrachloride, with a small amount of phosgene present.

Dilling and Dilling (1967) reported that the most probable mode of fragmentation of the mirex molecule is to hexachlorocyclopentadiene. However, neither our work nor the

previous work of McBee et al. (1956) or Eaton et al. (1960) indicated appreciable amounts of hexachlorocyclopentadiene to be present in the pyrolyzed mirex samples. The absence of hexachlorocyclopentadiene probably was the result of its further reaction. In our experiments, hexachlorobenzene was a major product detected when the residue resulting from pyrolysis of hexachlorocyclopentadiene at 500° was chromatographed on the OV-17, QF-1 column. Thus, at temperatures of 525° and above, hexachlorocyclopentadiene would probably be rapidly converted to hexachlorobenzene and would exist for only a short time in the ampule. The mechanism for the pyrolysis is being further investigated.

The atmosphere within the ampule had little, if any, effect on the thermal degradation of mirex. Helium, nitrogen, and oxygen atmospheres all led to the same products in the residue.

Sample size per unit volume was found to affect the chromatogram. The gas chromatogram resulting from 0.001 g of mirex heated to 550° in a 10-ml ampule contained only three peaks. Two of these peaks were identified as hexachlorocyclopentadiene and hexachlorobenzene (OV-17, QF-1 column), whereas the third one was very small with the same retention time as peak 1 ($t_R = 0.004$), previously described. The late eluting peak ($t_R = 0.207$) was absent from the chromatogram of the 0.001-g sample.

Samples heated above 650° in sealed vycor tubes showed appreciable carbonaceous material. However, of the residue soluble in hexane, hexachlorobenzene persisted as the dominant material present. Above 650°, the late eluting peak ($t_R = 0.207$) was again absent from the chromatogram obtained with the OV-17, QF-1 column.

LITERATURE CITED

- Alley, E. G., *J. Environ. Qual.* **2**, 52 (1973).
 Alley, E. G., Dollar, D. A., Layton, B. R., Minyard, J. P., Jr., *J. Agric. Food Chem.* **21**, 138 (1973).
 Alley, E. G., Layton, B. R., Minyard, J. P., Jr., *J. Agric. Food Chem.* **22**, 442 (1974).
 Dilling, W. L., Braendlin, H. P., McBee, E. T., *Tetrahedron* **23**, 1211 (1967).
 Dilling, W. L., Dilling, M. L., *Tetrahedron* **23**, 1225 (1967).
 Eaton, P., Carlson, E., Lombardo, P., Yates, P., *J. Org. Chem.* **25**, 1225 (1960).
 Gordon, S., McBride, B. J., Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations, NASA, SP-273, 1971.
 McBee, E. T., Roberts, C. W., Idol, J. D., Jr., Earle, R. H., *J. Am. Chem. Soc.* **78**, 1511 (1956).

Miles E. Holloman¹
 Bobby R. Layton²
 Maurice V. Kennedy*¹
 Charles R. Swanson³

¹ Department of Biochemistry

Mississippi State University
 Mississippi State, Mississippi 39762

² Mississippi State Chemical Laboratory
 Mississippi State, Mississippi 39762

³ Agricultural Research Service
 U.S. Department of Agriculture
 Stoneville, Mississippi 38776

Received for review February 10, 1975. Accepted June 11, 1975. This study was supported by Agricultural Research Service, U.S. Department of Agriculture, Cooperative Agreement No. 12-14-7001-108. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or the Mississippi Agricultural and Forestry Experiment Station and does not imply its approval to the exclusion of other products that may also be suitable.