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Reduction of Methyl Parathion Residues on Clothing by Delayed Field Re-Entry and Laundering

E. L. Finley[1], J. B. Graves[2], F. C. Hewitt[2], H. F. Morris[3], C. W. Harmon[3], F. A. Iddings[4], P. E. Schilling[5], and K. L. Koonce[5]

[1]School of Home Economics, [2]Department of Entomology, [3]Feed and Fertilizer Laboratory, [4]Nuclear Science Center, and [5]Department of Experimental Statistics, Louisiana State University of Agricultural Experiment Station, Baton Rouge, LA. 70803

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) is a fungicide used to protect a large number of agricultural crops, especially vegetables, from diseases.

As chlorothalonil is readily soluble in benzene, the latter had been used as the solvent in analyzing chlorothalonil residues in soil and crops. It was found, however, that when a sunlight-exposed benzene solution of chlorothalonil was injected into a gas chromatograph, it gave a lower response to a gas chromatographic detector than did an unexposed one and gave a new peak, representing an unknown substance, on the chromatogram.

As regards organochlorine pesticides, the reaction between dichlone and benzene (WHITE et al. 1969) as well as that between heptachlor and cyclohexane (MCGUIRE et al. 1970) have been reported. Since benzene appeared to have something to do with formation of the unknown substance, the author investigated into relations between chlorothalonil and solvents.

This report, originally presented at the meeting of the Agricultural Chemical Society of Japan at Sapporo, July, 1975, deals with the author's investigation.

EXPERIMENTAL

1) Equipment used

- Gas chromatograph: Shimadzu GC-5APTFE equipped with a ^{63}Ni detector and 3mm x 2m glass column packed with 3% OV-17 on 80/100 mesh Gas Chrom Q
- Gas chromatograph - Mass spectrometer: Hitachi RMU-6L; 3mm x 1m glass column packed with 10% SE-30 on 60/80 mesh Chromosorb W
- ^{13}C-Nuclear Magnetic Resonance: Varian CFT-20; frequency 20MHz; solvent $CDCl_3$

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2) Decrease in quantity of chlorothalonile in solvent

Acetone, n-hexane and benzene solutions of chlorothalonil (1 ppm) were prepared and each was introduced into a 20-mL boro-silicate test tube. After being stoppered, the test tubes were divided into two groups, those in the first group being directly exposed to the summer midday sunlight (about 100,000 lux), and the second group placed in a room near a window (about 6,000 lux). The test tubes were taken out one at a time from each group to measure the chlorothalonil with a gas chromatograph.

3) Investigation of suitable solvents for residue analysis of chlorothalonil

About 40 solvents were tested. In each case, a 4-ppm solution of chlorothalonil was prepared and the residual quantity of chlorothalonil was measured with an ECD-GC after the solution was exposed to a UV lamp for 60 min.

4) Identification of reaction product ion benzene solution of chlorothalonil

A sunlight exposed benzene solution of chlorothalonil was concentrated and injected into a gas chromatograph-mass spectrometer.

The reaction product was isolated, purified by silica-gel thin-layer chromatography, and was subjected to elementary analysis and ^{13}C-nuclear magnetic resonance.

RESULTS AND DISCUSSION

As Fig. 1 shows, the chlorothalonil (1 ppm) in the benzene disappeared completely in about 30 min. when the solution was directly exposed to the sun and reduced by more than 20% in about 150 min when the solution was placed near a window. In the meantime, chlorothalonil was found to be stable in acetone but weakly stable in n-hexane when exposed to the sun.

When exposed to an ultraviolet lamp (TABLE 1), chlorothalonil was found to react with hydrocarbons, alcohols and ethers but not with ketones, esters and halogenated hydrocarbons. Hence, it is believed that residue analysis of chlorothalonil should be performed using the latter solvents.

As a result of GC-MS analysis of benzene-chlorothalonil reaction product (Fig. 2), a cluster of molecule ion peaks, which is characteristic of a substance containing three chlorine atoms, was detected at above m/e 306.

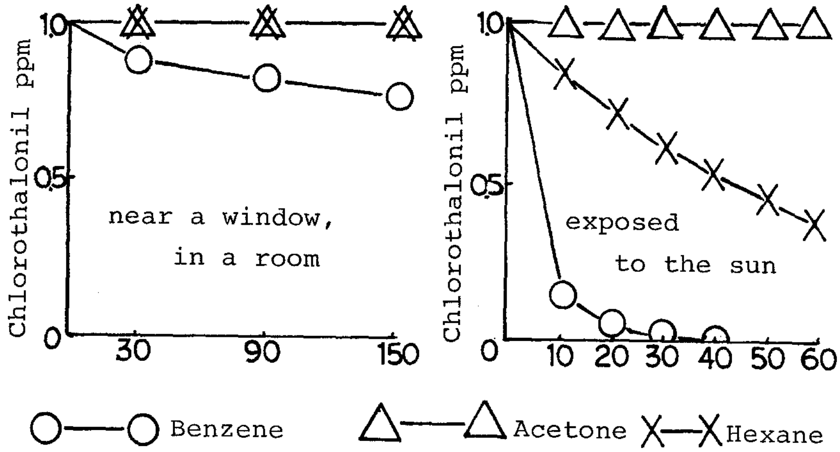

Fig. 1 Decrease in Quantity of Chlorothalonil in Organic Solvents

TABLE 1
Stability of Chlorothalonil in Solvents
Exposed to Ultraviolet Lamp

Stable	Weakly Stable	Unstable
Acetone	DMSO	Benzene
Acetonitrile	Epichlorohydrin	n-Butanol
Carbon disulfide	Isoamyl acetate	Cyclohexane
Carbon tetrachloride	Isooctane	Cyclohexanol
Chloroform	Methanol	Dichloromethane
Cyclohexanone		Dimethylacetamide
Divinylbenzene		Dimethylformamide
Ethyl acetate		Dioxane
Mesityl oxide		Ethanol
Methyl bromide		Ethyl ether
Methyl ethyl ketone		n-Heptane
Methyl isobutyl ketone		n-Hexane
Nitromethane		Isopropyl ether
Tetrachlorodifuloroethane		n-Pentanol
		Propylene oxide
		Tetrahydrofuran
		Toluene
		Xylene (o-, m-, p-)

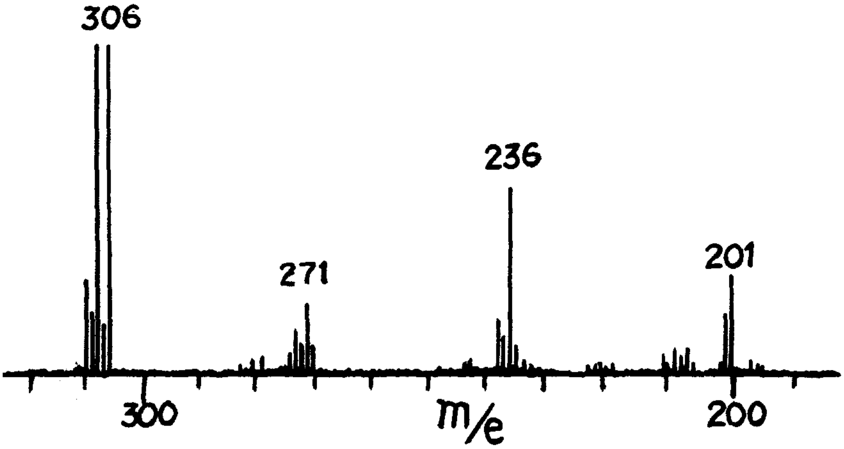

Fig. 2 Mass Spectrum of Photochemical Reaction Product of Chlorothalonil in Benzene

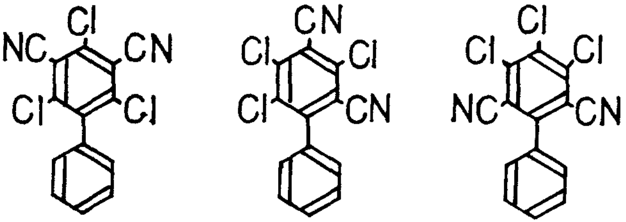

Fig. 3 Possible Structure of a Compound Formed by Replacement of a Chlorine Atom of Chlorothalonil with a Phenyl radical

These findings, together with the result of elemental analysis (Found C: 54.0, H: 1.40, N: 8.99; Calculated for $C_{14}H_5Cl_3N_2$, C: 54.7, H: 1.64, N: 9.01; melting point 195-196°C), indicate that the reaction product has the molecule formula of $C_{14}H_5Cl_3N_2$ and that it has been formed by replacement of one of Cl atoms of chlorothalonil with a phenyl radical (Fig. 3).

To determine the substitution position of chlorothalonil, analysis were performed with ^{13}C-NMR, giving attention to whether the structure is symmetrical (types 1 and 3) or asymmetrical (type 2). If it were a symmetrical biphenyl, the ^{13}C-NMR spectrum of the reaction product should have produced one peak each for $\rangle\dot{C}$-CN and $\rangle C$-$\dot{C}N$ and two peaks for $\rangle\dot{C}$-Cl, but, as it turned out, the spectrum produced two peaks each for $\gg\dot{C}$-CN and $\gg C\text{-}\dot{C}N$ and three peaks for $\gg\dot{C}$-Cl as per Fig. 4. It was, therefore, concluded that the reaction product was 3,5,6-trichlorobiphenyl-2,4-dicarbonnitrile of the asymmetrical type 2.

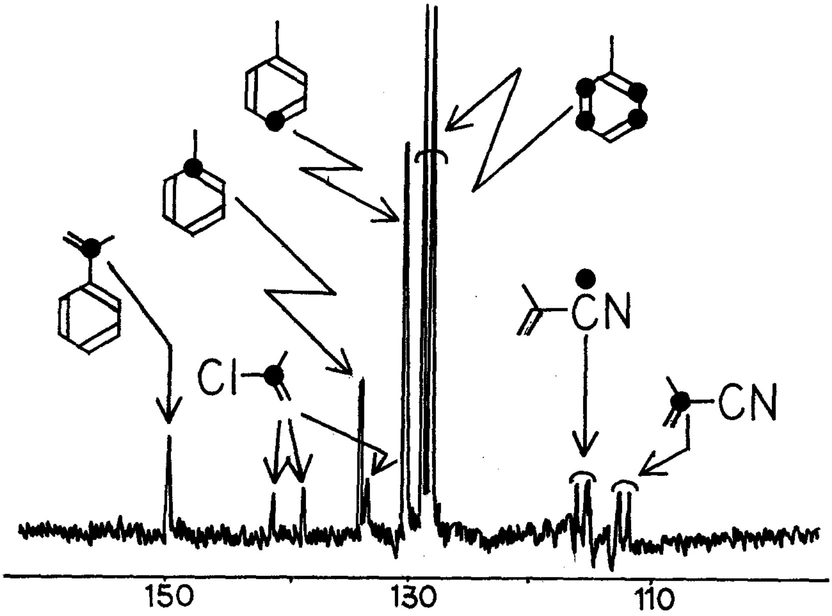

Fig. 4 ^{13}C-NMR Spectrum of Photochemical Reaction Product

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