To illustrate the utility with the mass spectra, categories that were known to be linearly separable when all mass peaks greater than 0.5% were used were made inseparable by retention of only the 6 largest peaks in each spectrum. That is, the pattern set consisted of 630 spectra, each containing only the six most intense peaks in its mass spectrum.

Surprisingly, most of the questions tried using only the 6 largest peaks were linearly separable and the two examples listed in Table IV were the only ones by which the use of a negative delta was required. However these adequately

prove the superiority of the delta approach when compared with the threshold logic unit. In each case prediction is considerably better with the use of a no-decision region. The results for a C/H ratio of 1/2 are particularly striking, especially the difference between negative categories (93.4% with delta as opposed to 72.7% without delta).

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Systematic Studies on the Breakdown of *p*,*p*'-DDT in Tobacco Smokes

II. Isolation and Identification of Degradation Products from the Pyrolysis of $p_{,p'}$ -DDT in a Nitrogen Atmosphere

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p,p'-DDT was pyrolyzed at 900 °C in a nitrogen atmosphere and the pyrolysis products were collected in pentane at -80 °C and isolated by fractional distillation and chromatography on alumina and Florisil columns. The products isolated were: p,p'-DDT, p,p'-DDE, p,p'-TDE, bis-(p-chlorophenyl)chloromethane, bis-(pchlorophenyl)methane, p,p'-dichlorobiphenyl, α,p dichlorotoluene, hexachloroethane, chlorobenzene, tetrachloroethylene, trichloroethylene, carbon tetrachloride, chloroform, and dichloromethane. The solid (first 8) pyrolysis products were identified by gas chromatography and IR spectrometry, and the liquid (the last 6) pyrolysis products were identified by gas chromatography and colorimetric tests. Besides these pyrolysis products p,p'-DDM, and cis- and trans-p,p'dichlorostilbenes were also detected in the pyrolyzate. As they were present in small quantities they were not isolated but were identified by gas chromatography.

IN THE FALL of 1967 we embarked upon a systematic investigation into the breakdown of p,p'-DDT in cigarette main-stream and side-stream amokes. This is the first study of its kind and is divided into three phases—the study of the breakdown of p,p'-DDT in a nitrogen atmosphere, in p,p'-DDT treated tobacco smokes, and in the cigarette main-stream and sidestream smokes. So far we have written two papers on the results and mechanisms of the breakdown of p,p'-DDT in a nitrogen atmosphere, and in p,p'-DDT treated tobacco smokes (1, 2).

In the first phase our objective was to study, from the breakdown of p,p'-DDT in an inert atmosphere such as nitrogen, the mechanisms of the breakdown of p,p'-DDT at 900 °C—

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the temperature of the on-puff burning zone of cigarette (3). In this study the temperature was the only parameter which corresponded to the smoking condition of a cigarette. Our choice of an inert atmosphere turned out to be fortunate since we later on found (2) that the atmosphere where the pyrolysis of pesticide takes place is inert.

The results of our work on the first phase are described in our first paper (1) in Section 1. In the present paper we are reporting the methods employed in the pyrolysis of p,p'-DDT, and the isolation and identification of its pyrolysis products. The products reported are: p,p'-DDT [2,2-di-(p-chlorophenyl)-1,1,1-trichloroethane] and compounds with smaller molecular weight such as; p,p'-DDE [2,2-di-(p-chlorophenyl)-1,1-dichloroethylene], p,p'-TDE [2,2-di-(p-chlorophenyl)-1,1-dichloroethylene], cis- and trans-4,4'-dichlorostilbenes, bis-(p-chlorophenyl)methane, bis-(p-chlorophenyl)-chloroethylene], cis- and trans-4,4'-dichlorostilbenes, bis-(p-chlorophenyl)methane, bis-(p-chlorophenyl)-chloroethylene, carbon tetrachloroethylene, carbon tetrachloride, chloroform, and dichloromethane.

EXPERIMENTAL

Materials. All solvents used were of "pure" grade, and were distilled before use. ("Pure" and "Puriss" grades refer to the quality of the reagent as mentioned on the reagent bottle. "Puriss" grade was 99.9%+ pure.) p,p'-DDT used for pyrolysis was of "Puriss" grade, and was purchased from Aldrich Chemical Co.

ALUMINA AND FLORISIL. Alcoa chromatographic alumina F-20 was purchased from Aluminum Company of America, and Florisil (mesh, 100-200) was purchased from Fisher. These were activated as described in the text.

REFERENCE COMPOUNDS. p,p'-DDT (99.9% + pure) and p,p'-DDE (99.8% pure) were obtained from Geigy

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Figure 1. Infrared spectrum of bis-(p-chlorophenyl)chloromethane in KBr



Figure 2. Pyrolysis apparatus

Chemical Corp., and p,p'-TDE (pure) was obtained from Rohm and Haas.

4,4'-Dichlorobiphenyl was purchased from Chemical Procurement Laboratories. It was crystallized from pentane. The purified product had an IR spectrum identical with that of 4,4'-dichlorobiphenyl as reported in literature (4).

Bis-(p-chlorophenyl)methane, α ,p-dichlorotoluene, and hexachloroethane were purchased from Eastman Organic Chemicals. They were crystallized from pentane. Their purified products had IR spectra identical with those of bis-(p-chlorophenyl)methane (5), α ,p-dichlorotoluene (6), and hexachloroethane (7), respectively.

Carbon tetrachloride, chlorobenzene, chloroform, dichloromethane, tetrachloroethylene, and trichloroethylene were of the purest grade available in the market. They were tested for purity, and purified wherever necessary.

p,p'-DDM (p,p'-TDEE) was synthesized from pure p,p'-TDE (20 g) by refluxing it with excess of alcoholic KOH for 24 hours [*cf.* Haller *et al.* (8)]. The reaction product was crystallized from isopropanol. Its melting point, 66–67 °C and IR spectrum were identical with those reported for p,p'-DDM (5).

Bis-(p-chlorophenyl)chloromethane was prepared by passing dry HCl through a solution of p,p'-dichlorobenzhydrol (5 g) in benzene (50 ml) for 6 hours. The benzene solution was then evaporated to dryness under reduced pressure. The resulting yellowish oily residue solidified on standing. It was dissolved in pentane and treated with activated charcoal. The solution was then filtered and concentrated when white crystals of the crude product appeared. These crystals were recrystallized from pentane to give pure bis-(p-chlorophenyl)chloromethane, mp 62–63 °C (9). Anal. Calculated for $C_{13}H_9Cl_3$: C, 57.4; H, 3.32; Cl, 39.22. Found: C, 57.27; H, 3.35; Cl, 39.10. Its IR spectrum is shown in Figure 1.

Trans-4,4'-dichlorostilbene was synthesized according to the method of Hoffmann and Rathkamp. The melting point, 176.5–177 °C, and the IR spectrum of the purified product was identical with that of trans-4,4'-dichlorostilbene (10).

Methods. PYROLYSIS OF p,p'-DDT. The pyrolysis apparatus is shown in Figure 2. It consisted of three sections: a hopper unit, the pyrolysis tube, and traps. The hopper unit and traps were made of glass, and the pyrolysis tube was made of quartz. All the connections in the apparatus were glass to glass.

p,p'-DDT (10 g) was introduced into tube (T) of the hopper and stoppered. From there it was introduced into the pyrolysis tube (PT) with a glass piston. From the other end of the hopper, nitrogen was introduced into the tube at the rate of 150 ml/min. The pyrolysis tube, 50 cm \times 2.5 cm in diameter, had an indentation in the middle of which a 2-cm thick bed of broken quartz pieces (BQ) rested. The pyrolysis tube was heated in a muffle furnace to 900 °C. Small quantities of p,p'-DDT were dropped on a red hot broken quartz bed over a period of about 2 hours. The escaping pyrolysis products were trapped in five traps. The first trap was empty and was cooled to 0 °C. The other traps contained about 30 ml of pentane, and were cooled to -80 °C.

^{(4) &}quot;Sadtler Standard Spectra," Midget ed., Sadtler Res. Lab., Philadelphia, 1962, No. 15044.

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Pentane Extract (PE).



Figure 3. Procedure for isolation of pyrolysis products of $p_{,p}$ '-DDT



Figure 4. GLC chromatogram of PED on a 3% SE 30 column

- 1. Pentane
- 5. Trichloroethylene
- 2. Dichloromethane
- Tetrachloroethylene
 Chlorobenzene
- 3. Chloroform7.4. Carbon tetrachloride8.
 - 8. Hexachloroethane

After the pyrolysis operation was over, the pentane solutions in the traps were combined and the residue left in each trap was extracted with 20 ml of pentane. The pentane solutions and extracts were combined and filtered, and the filterate (PE) processed as shown in Figure 3.

PE was worked up into three fractions: Pentane Reflux

volatile Fraction (NVF). PE was refluxed with ice-cold water passing through the reflux condenser. The escaping gases were trapped in a

pentane trap at -80 °C to give PRF. The PE, after the removal of PRF, was distilled on a water bath at 50 °C to give a viscous yellowish brown solid residue, NVF (0.155 g), and the distillate PED. The gas chromatograms of the PED and NVF are shown in Figures 4 and 5.

Fraction (PRF), Pentane Extract Distillate (PED), and Non-

The chromatograms show that excluding the solvent there are 7 substances present in the PED and 20 substances in the NVF.

ISOLATION OF PYROLYSIS PRODUCTS. PED was slowly fractionally distilled in two stages. In the first stage, three 30-cm long Snyder fractionating columns were used and $1/_3$ volume of the distillate (DI) was collected; and in the second stage the remaining liquid in the flask was fractionally distilled three times with only one Snyder column till about 10 ml of the residue was left in the flask. The distillate was designated as DII, and the residue as RI. DI, DII, and RI were gas chromatographically found to contain 2, 2, and 4 substances, respectively. DI was concentrated by fractional distillation with three Snyder columns: the concentrate consisted of the first 25 ml of the distillate. DII was concentrated by fractional distillation with four Snyder columns: the concentrate, about 10 ml, was left in the flask.



- 1. Pentane
- 2. Hexachloroethane
- 3. α , *p*-Dichlorotoluene
- 4. p, p'-Dichlorobiphenyl
- 5. Bis-(p-chlorophenyl)methane
- 6. Cis-p,p'-dichlorostilbene
- 7. Bis-(p-chlorophenyl)chloromethane
- 8. *p*,*p*'-DDM
- 9. p,p'-DDE and trans-p,p'-dichlorostilbene
- **10.** *p*,*p*'-**TD**E
- 11. *p*,*p*'-DDT



Concentrated DI and DII, RI, and NVF were chromatographed on suitable columns equipped with a fraction collector. In all the chromatographs, the rate of flow of the eluent was 1 ml per minute.

Concentrated DI (5-ml aliquot) was chromatographed on a 25 cm \times 1.5 cm diameter activated alumina column (alumina was activated at 110 °C for 16 hours) with pentane as an eluent. Sixty 3-ml fractions were collected. These fractions, when examined gas chromatographically, showed the presence of two substances. The first substance appeared in fractions 13–17, and the second in fractions 38–45. These fractions were combined to give F1 (fractions 13–17), and F2 (fractions 38–45).

Concentrated DII (2-ml aliquot) was chromatographed on a 60 cm \times 1.5 cm diameter activated alumina column (alumina activated at 250° for 16 hours) with pentane as an eluent. One hundred 3-ml fractions were collected. These fractions, when examined gas chromatographically, were found to contain two substances spread over fractions 25-41 and 45-65, respectively. These fractions were combined to give F3 (fractions 25-41), and F4 (fractions 45-65).

RI (2-ml aliquot) was chromatographed on a column identical with that used for DII. Pentane was used as an eluent and one hundred and fifty 2-ml fractions were collected. When examined gas chromatographically fractions 25-45 60-100, and 130-150 were found to contain one, three, and two substances, respectively. These fractions were combined to give F5 (fractions 20-45), FA (fractions 60-100), and FB (fractions 130-150). FA was carefully fractionally distilled with one Snyder column until 5 ml of liquid was left in the distillation flask. The distillate was examined gas chromatographically and was found to contain the same substance as found in F4. The residue was rechromatographed on a 60 cm \times 1.5 cm diameter activated alumina column (alumina activated at 250 °C). Fractions 25-50 were found to contain the same substance as in F5. Fractions 75-100 were found to contain one substance. They were combined to give F7. Fractions 51-74 contained two substances one of which was present in traces. This substance was found to be the same as that present in F7. The combined fractions 51-74 were designated as F6. FB was similarly rechromatographed to give F6 and F7.

NVF (0.15 g) was chromatographed on a 50 cm \times 5 cm diameter activated Florisil column (Florisil activated at 110 °C for 16 hours) with 10 liters of hexane followed by 8 liters of 1% ether in hexane as eluent. Eight hundred 20-ml fractions were collected. These fractions, when examined gas chromatographically, showed that a partial separation of the various constituents of the NVF was achieved. Fractions containing the same dominant single substance were combined and repeatedly rechromatographed till fractions containing the single dominant substance were obtained. Thus fractions 18-25, 35-50, 175-270, 310-335, 425-500, 600-625, 690-720, and 770-800 gave fractions F7, F8, F9, F10, F11, F12, F13, and F14. The F7 obtained contained the same substance as the F7 from RI.

Methods of Detection. GAS CHROMATOGRAPHY. A Micro Tek MT-220 gas chromatograph equipped with a ⁶³Ni electron capture detector, and a Dohrmann Model C-200 microcoulometer with a Model S-100 combustion unit were employed in this study. The three columns A, B, and C used were 6 ft \times ¹/₄-inch diameter glass columns. Column A was packed with 3% SE 30 on 80–90 mesh Chromoport XXX; column B with 5% SE 30 on 80–90 mesh Chromoport XXX; and column C with 20% Carbowax 20 M on 80–100 mesh Chromoport XXX. The column temperatures and gas flow varied depending upon the compound being investigated.

COLORIMETRIC TESTS. Colorimetric tests were done only on the constituents of the PED. Since all of the compounds were in pentane solutions, tests used in their detection had to be modified from what they were reported in literature. For chlorobenzene, a new test was developed in our laboratory. The colorimetric tests employed are as follows.

Test 1. Dichloromethane was detected by a method based on that by Gronsberg (11). A mixture of 1 ml of the sample and 2 ml of 20% ethanolic KOH was refluxed for 1 hour. The reaction mixture was cooled and then added to 3 ml of sulfuric acid containing 0.1–0.2 g of chromotropic acid. A violet color indicated the presence of dichloromethane (detection limit 5 μ g). Carbon tetrachloride, chloroform, 1,2dichloroethane, 1,1,2,2-tetrachloroethane, tetrachloroethylene, and trichloroethylene gave no color.

Test 2. Chloroform and trichloroethylene were tested by a modification of Fujiwara test as reported by Feigl (12). Five drops each of 20% NaOH and pyridine, and 0.5 ml of the test solution were heated at 100 °C for 1–2 minutes. To the red colored solution which was formed 3–4 crystals (*ca.* 1 mg) of benzidine hydrochloride were added and the solution acidified with acetic acid. Chloroform (detection limit, 2 μ g) and trichloroethylene (detection limit, 5 μ g) gave a violet color with this method, while dichloromethane (detection limit, 500 μ g) gave a pink color. Tetrachloroethylene and hexachloroethane gave no color.

Test 3. Chloroform and trichloroethylene were also tested by a modification of Brumbaugh and Stallard's method (13). A mixture of 1 ml each of aniline and pyridine were refluxed with 2 ml of the sample at 135–140 °C for 15 minutes, and then 2 drops of 5% methanolic KOH were added. Chloroform and trichloroethylene gave a yellow-orange color. Tetrachloroethylene gave the color on further refluxing, while carbon tetrachloride and dichloromethane gave no color. The detection limits both for chloroform and trichloroethylene were 50 μ g.

Chloroform was distinguished from trichloroethylene by heating the aniline-pyridine-sample mixture at 50 °C. Under these conditions only chloroform gave the color.

Test 4. Carbon tetrachloride and chloroform were detected by a modification of Belyakov's method (14). One milliliter each of pyridine and the test sample, and 2 drops of 1.0N NaOH were refluxed at 100 °C till a pink or red color developed (maximum time, 30 minutes). The colored solution was cooled and 3-4 drops of aniline and 1 ml of glacial acetic acid were added. Carbon tetrachloride and chloroform gave a yellowish orange color (detection limit for each, 5 μ g). Dichloromethane gave no color.

Test 5. Chlorobenzene was detected by its conversion to aniline with potassium amide in liquid ammonia according to the method of Chopra and Domanski (15). Potassium metal (50 mg) was added to a dry 3-neck flask connected to nitrogen and ammonia tanks, and fitted with a dropping funnel and a Dewar condenser containing solid CO_2 and acetone. Ammonia was passed through the flask till about 50 ml of liquid ammonia was collected in the flask. A small amount of ferric nitrate was added as a catalyst. The reaction mixture was stirred vigorously till the original blue color of the reaction mixture turned gray. A pentane solution of the sample (*ca.* 10 ml) was then added. After 5 minutes the reaction was quenched by adding an excess of ammonium bromide, and liquid ammonia was allowed

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T	abie I.	Identification	of various	Pyrolysis	Products II	n PED Irol	n the Pyro	iysis oi p,p		a Nitrogen	Atmosphere
Frac- tion	No. of com- pounds present	Reference compound	Results of cochromatography with reference compounds and with E.C. and micro- coulometric detectors			Results of colorimetric tests and their comparison with reference compounds					Identification of the unknown
No.			Column A	Column B	Column C	Test 1	Test 2	Test 3	Test 4	Test 5	compound
F 1	One	Dichloro- methane	No sep- aration	No sep- aration	No sep- aration	violet SARC ^a	Pink SARC ^a	No color SARC ^a	No color SARC ^a		Dichloromethane
F2	One	Chloroform	No sep- aration	No sep- aration	No sep- aration	No color SARC	violet SARC	yellow orange SARC	Yellow orange SARC	•••	Chloroform
F3	One	Carbon tetra- chloride	No sep- aration	No sep- aration	No sep- aration	No color SARC	Pink SARC	No color SARC	yellow orange SARC		Carbon tetrachloride
F4	One	Trichloro- ethylene	No sep- aration	No sep- aration	No sep- aration	No color SARC	violet SARC	yellow orange SARC			Trichloro- ethylene
F5	One	Tetrachlo- roethylene	No sep- aration	No sep- aration	No sep- aration	No color SARC	No color	yellow orange SARC			Tetrachloro- ethylene
F6	Two	Chloro- benzene	No sep- aration	No sep- aration	No sep- aration				•••	Orange spots with R _f	Chlorobenzene
		Hexachloroethane (see F7, Table 2)							SARC		
ª Sa	me as ref	erence compou	ind.								

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Table II. Identification of Various Pyrolysis Products in NVF from the Pyrolysis of p, p'-DDT in a Nitrogen Atmosphere

Fraction	No. of compounds		Results of cocl with referenc and with microcoulome	hromatography e compounds E.C. and etric detectors	Comparison of the IR spectra of the unknown with that of the	Identification of
No.	present	Reference compound	Column A	Column B	reference	the unknown compound
F 7	One	Hexachloroethane	SARC ^a	SARC ^a	\mathbf{SARC}^{a}	Hexachloroethane
F8	One	α, p -Dichlorotoluene	$SARC^{a}$	SARC ^a	$SARC^{a}$	α , <i>p</i> -dichlorotoluene
F9	One	<i>p,p'-</i> Dichloro- biphenyl	SARC ^a	SARC ^a	SARC ^a	p,p'-dichlorobiphenyl
F10	One	Bis-(p-chlorophenyl)- methane	SARC ^a	SARC ^a	SARC ^a	Bis-(p-chlorophenyl)methane
F11	One	Bis(p-chlorophenyl)- chloromethane	SARC ^a	SARC ^a	SARC ^a	Bis-(<i>p</i> -chlorophenyl)- chloromethane
F12	One	p,p'-DDE	SARC ^a	SARC ^a	SARC ^a	p,p'-DDE
F13	One	p,p'-TDE	SARC ^a	SARC ^a	SARC ^a	p,p'-TDE
F14	One	p,p'-DDT	SARC ^a	SARC ^a	SARC ^a	<i>p,p'</i> -DDT
^a Same a	as reference con	npound.				

to evaporate. The residue, now containing aniline, was extracted with ether and the ether extract concentrated to 0.5 ml, and chromatographed on silica gel ITLC plates along with aniline as reference, and with chloroform as a mobile phase. The chromatograms were developed by spraying them with a solution containing 2 g α -naphthol, 10 ml of 25% triethylamine, and 90 ml of methanol, followed by the exposure of the chromatograms to nitric oxide fumes. The presence of chlorobenzene in the test sample was indicated by a spot of same color and R_f value as the reference spot.

RESULTS

The results of the experiments for the isolation and identification of various pyrolysis products obtained from the pyrolysis of p,p'-DDT in a nitrogen atmosphere are shown in Tables I and II. Table I shows the compounds present in the PED, and Table II, in the NVF.

The two tables confirm the presence of 14 compounds in the p,p'-DDT pyrolysis products. Three more compounds:

p,p'-DDM, and *cis*- and *trans*-dichlorostilbenes were not isolated since they were present in very small amounts. However, their presence was shown by their cochromatography with reference compounds on columns A and B with E.C. and microcoulometric detectors.

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