

Systematic Studies on the Breakdown of Endosulfan in Tobacco Smokes: Isolation and Identification of the Degradation Products from the Pyrolysis of Endosulfan I in a Nitrogen Atmosphere

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With the objective of studying the possible degradation products of endosulfan in endosulfan-treated tobacco smoke, endosulfan I was pyrolyzed at 880–900 °C. Among the pyrolysate endosulfan I and II, endosulfan ether, hexachlorocyclopentadiene, all chlorobenzenes, methyl chloride, dichloromethane, chloroform, carbon tetrachloride, 1,1-dichloroethylene, 1,1-dichloroethane, trichloroethylene, and tetrachloroethylene were identified. From the reaction mechanisms involved in the formation of these compounds it is postulated that the endosulfan degradation products, which have a mathematical chance of being present in tobacco and cigarette smokes, are: endosulfan I and II, endosulfan sulfate, endosulfan ether, endosulfan lactone, mono-, di-, tri-, and tetrachlorobenzenes, and hexachlorocyclopentadiene.

This is our third paper on our investigations into the fate of endosulfan in tobacco and in cigarette smoke. In our earlier publications we had described the fate of endosulfan I and II and endosulfan sulfate in green tobacco leaf (Chopra and Mahfouz, 1977a) and in cured tobacco leaf (Chopra and Mahfouz, 1977b).

In 1970 we pioneered the use of a systematic study on the pyrolysis of pesticides at 900 °C in a nitrogen atmosphere as a method for predicting the fate of pesticides in tobacco and cigarette smokes (Chopra et al., 1970; Chopra, 1972). The studies included the isolation and identification of the pesticide breakdown products and the mechanisms of their formation. From the data so obtained, and the data obtained on the composition of tobacco smoke, it is possible to predict the fate of pesticides in tobacco and cigarette smokes. We carried out studies on the pyrolysis of *p,p'*-DDT in a nitrogen atmosphere, and our subsequent work (Chopra and Domanski, 1972; Chopra and Sherman, 1972; Chopra and Thekkekandam, 1973) showed that the *p,p'*-DDT degradation products in tobacco smoke could very well be predicted on the basis of our earlier results.

In 1973, with the objective of predetermining the possible endosulfan degradation products in tobacco we pyrolyzed endosulfan I in a nitrogen atmosphere at 900 °C and isolated and identified its degradation products. In this paper we are reporting our findings and interpretations on our investigations.

MATERIALS AND METHODS

Materials. All solvents used were of "pure" grade and were distilled before use. Endosulfan I and all the reference compounds were of 99%+ purity and were tested on GLC for purity before use.

Methods. Pyrolysis of endosulfan I (10 g) was carried out in a nitrogen atmosphere by dropping the pesticide in a quartz tube heated to 880–900 °C (for details, see Chopra and Osborne, 1971), and the pyrolysis products were collected in traps containing pentane cooled to 0 and –80 °C. After the pyrolysis, 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 filtrate, PE

(pentane extract), was processed as shown in Figure 1 (cf. Chopra and Osborne, 1971). For the detection of methyl chloride, heptane was used in place of pentane in the traps (cf. Chopra and Sherman, 1972).

The pyrolysis gases, which were not absorbed by pentane in the cold traps, were found to contain hydrogen chloride and sulfur dioxide. No hydrogen sulfide or sulfur trioxide (tested as sulfate) was detected in these gases.

Of all the pyrolysates only the yield of the nonvolatile fraction (NVF; yield, 1.4 g) was determined. The rest of the pyrolysates included liquid and gaseous products plus a large quantity of carbon.

Detection of the Pyrolysis Products. Pyrolysis products in distillate A (DA), distillate C (DC), residue A (RA), and nonvolatile fraction (NVF) were detected on GLC by their retention times and by cochromatographing them with authentic reference compounds. The presence of pyrolysis products with molecular weights of over 110 were confirmed by GC-MS. Since there was too much interference in the mass spectra region of 70 amu or less, meaningful studies on the mass spectra of compounds having molecular weights of less than 110 could not be made. The details of GLC and GC-MS systems used are given below.

Gas Chromatography. A Micro Tek MT-220 gas chromatographic unit equipped with a ⁶³Ni electron-capture and a Coulson electrolytic conductivity detector was employed in this study. The columns used were: (1) a 183 cm × 0.4 cm diameter glass column packed with 3% SE-30 on Chromport XXX (80–90 mesh), (2) a 183 cm × 0.2 cm diameter glass column packed with 3% OV-1 on Chromsorb W, and (3) a 183 cm × 0.4 cm diameter glass column packed with 5% QF-1 on Chromport XXX (mesh 60–80). The column temperatures and gas flow varied depending upon the compound being investigated.

GC-MS. The GC-MS used was a Finnigan 3100 F unit. The column used was a 183 cm × 0.2 cm diameter glass column packed with 3% OV-1 on Chromsorb W. The column temperatures and gas flow varied depending upon the compound being examined. The presence of any particular compound in the pyrolysate was confirmed by comparing its mass spectrum with that of the reference compound.

RESULTS

The results of the chromatography of DC, RA, and NVF are shown in Figures 2, 3, and 4. The chromatograph of residue B (RB) (not shown) showed the presence of the

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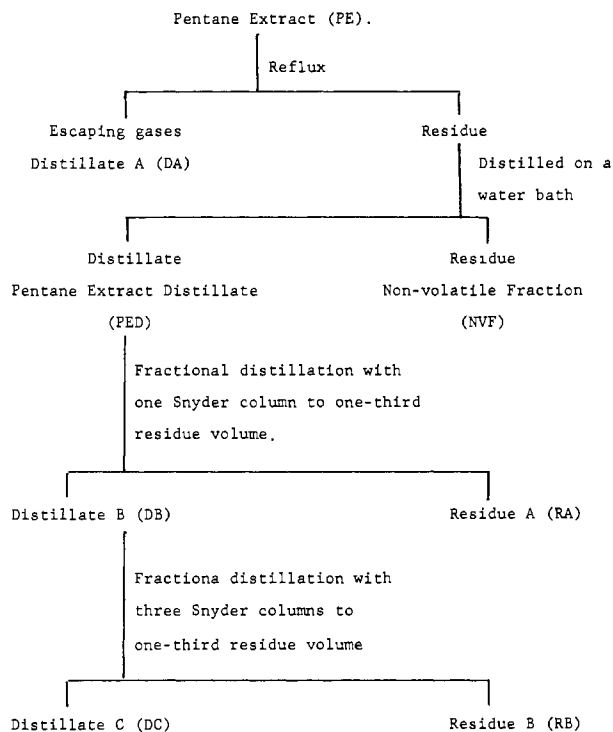


Figure 1. Procedure for the fractionation of the pentane extract (PE).

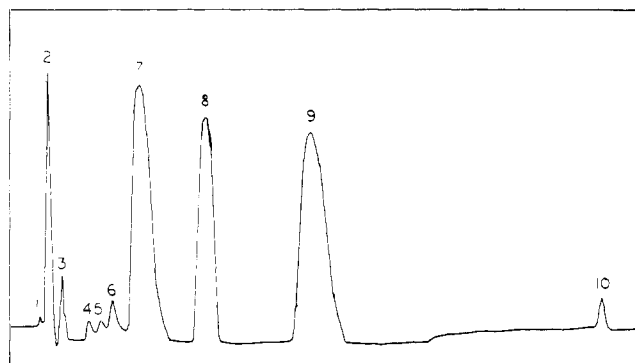


Figure 2. Gas chromatography of distillate C (DC) and the identification of compounds present in it: (1) methyl chloride, (2) solvent, (3) dichloromethane, (4) solvent, (5) 1,1-dichloroethylene, (6) 1,1-dichloroethane, (7) chloroform, (8) carbon tetrachloride, (9) trichloroethylene, (10) tetrachloroethylene. Column: 3% OV-1 on Chromsorb W; column temperature, 4 °C; nitrogen gas flow rate, 35 mL/min; detector, EC.

constituents of DC and RA. The escaping gases in DA showed the presence of methyl chloride.

Vinyl chloride, or chlorohydrocarbons containing three or four carbon atoms were not detected in any of the pyrolysate fractions.

The mass spectra of chlorobenzenes containing different numbers of chlorine atoms were different from each other, but were the same for all isomeric chlorobenzenes. Similarly, the GLC retention times for *m*- and *p*-dichlorobenzene and 1,2,3,5- and 1,2,4,5-tetrachlorobenzene were the same. It was, therefore, not possible to distinguish between *m*- or *p*-chlorobenzene, or between 1,2,3,5- and 1,2,4,5-tetrachlorobenzene.

Though these pyrolysis studies are qualitatively reproducible, quantitatively they are not. There are several factors which affect the yield of the pyrolysate; e.g., the exact temperature and geometry of the pyrolysis tube; the rates of the flow of nitrogen, and at which the pesticide is introduced into the pyrolysis tube, etc. Most of the

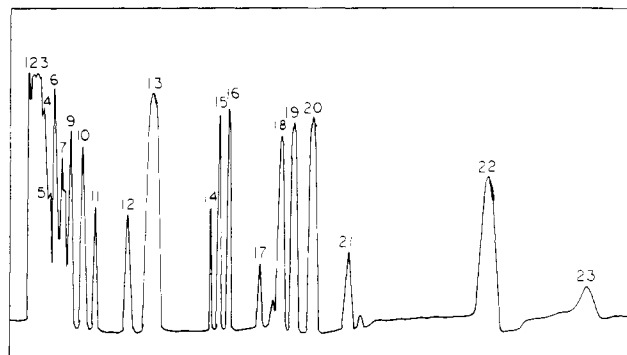


Figure 3. Gas chromatography of residue A (RA) and the identification of compounds present in it: (1-5) carry over from DC, (6) chlorobenzene, (7-11) unidentified compounds (possibly aromatic hydrocarbons), (12) *m*- and *p*-dichlorobenzene, (13) *o*-dichlorobenzene, (14) 1,3,5-trichlorobenzene, (15) 1,2,4-trichlorobenzene, (16) 1,2,3-trichlorobenzene, (17) unknown, (18) 1,2,3,5- and 1,2,4,5-tetrachlorobenzene, (19) hexachlorocyclopentadiene, (20) 1,2,3,4-tetrachlorobenzene, (21) unknown, (22) pentachlorobenzene, (23) unknown. Column, 3% OV-1 on Chromsorb W; column temperature, 80 °C; nitrogen gas flow rate, 35 mL/min; detector, EC. Hexachlorobenzene was identified in RA at column temperature 160 °C and gas flow rate 60 mL/min.

pyrolysis product was carbon: the yield of other pyrolysis products was small. These pyrolysates included solids, liquids, and gaseous products, and this made the determination of total yield very difficult, if not impossible. Further, since there may be several different routes by which a product may be formed, the estimation of its yield did not help much in the study of the mechanisms involved in its formation and as such was not of much use.

DISCUSSION

Pyrolysis reactions in an inert atmosphere involve three events: (1) the excitation of the molecule; (2) rearrangement of the excited molecule, or the breakdown of the excited molecule into fragments with the weakest bonds breaking preferentially; and (3) the rearrangement of the fragments produced, or the recombination of the fragments to produce various products including dimers and polymers. This may be seen in the pyrolysis of endosulfan I in the nitrogen atmosphere.

The endosulfan I pyrolysis products formed may be divided into four categories: (1) those in which the endosulfan I molecule has undergone a rearrangement reaction, namely, endosulfan II which is formed by the conversion of the sulfite moiety in endosulfan I from endo form to exo form in endosulfan II; (2) endosulfan ether, which is produced by the elimination of SO₂ from endosulfan molecule to form a stable tetrahydrofuran ring in endosulfan ether (see Figure 5); (3) hexachlorocyclopentadiene, which is a product of a reverse Diels-Alder reaction (cf. Kwart and King, 1968); and (4) the chlorobenzenes and chlorohydrocarbons containing one and two carbon atoms, such as, methyl chloride, dichloromethane, chloroform, carbon tetrachloride, 1,1-dichloroethylene, 1,1-dichloroethane, trichloroethylene, and tetrachloroethylene (see Figure 6), which are generated by cyclodehydration reactions (cf. Hoffmann, 1971) and the reactions of the fragments produced with each other. It is noteworthy that there are no chlorohydrocarbons containing three or four carbon atoms among them. Pentachloro- and hexachlorobenzene can be formed by the action of HCl or chlorine with tetrachlorobenzene formed during the pyrolysis (cf. Ballester and Santiago, 1974); 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes can be formed from 1,2,3,4-tetrachlorobenzene by the migration of chlorine

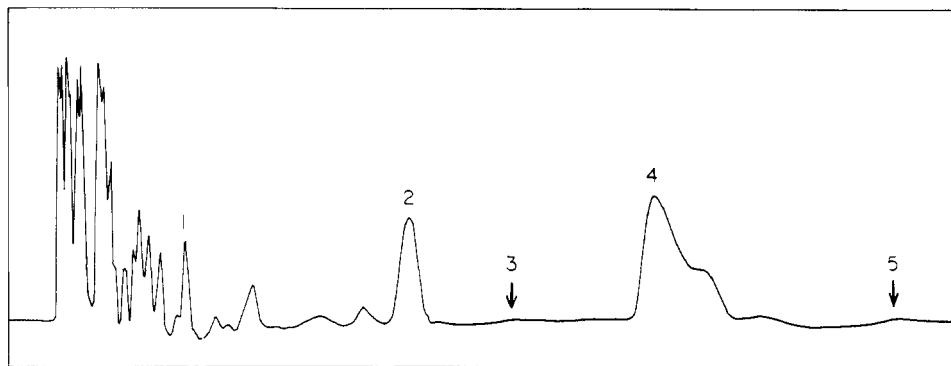


Figure 4. Gas chromatography of the nonvolatile Fraction (NVF) and the identification of the compounds present in it: (1) endosulfan ether, (2) endosulfan I, (3) position of the peak due to endosulfan lactone if present, (4) endosulfan II, (5) position of the peak due to endosulfan sulfate if present. Several of the peaks coming before endosulfan ether were also shown in RA. Column, 3% OV-1 on Chromsorb W; column temperature, 175 °C; nitrogen gas flow rate, 60 mL/min; detector, EC.

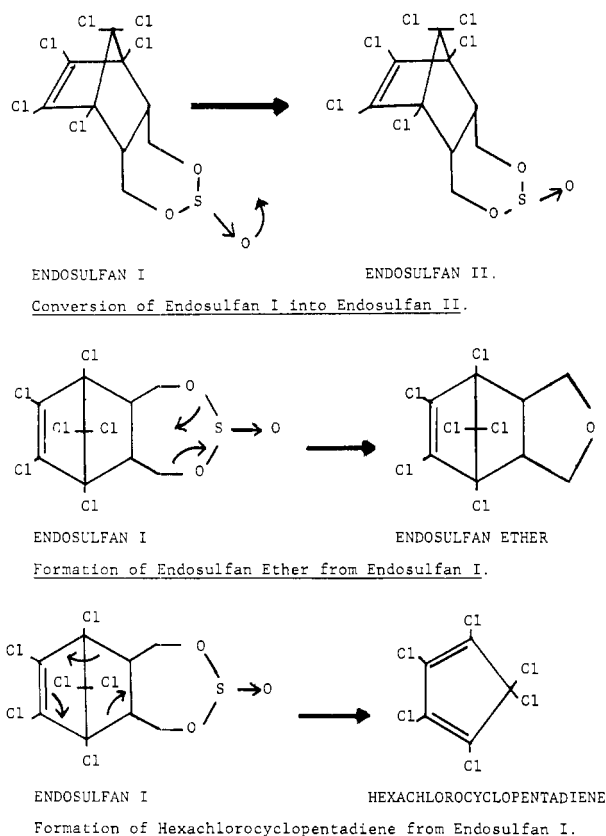


Figure 5. Mechanisms for the formation of endosulfan II, endosulfan ether, and hexachlorocyclopentadiene from endosulfan I.

atom(s); and mono-, di-, and trichlorobenzenes can be formed from the tetrachlorobenzenes by the loss of appropriate number of chlorine atoms.

In a highly reactive atmosphere, such as that present in tobacco pyrolysis zone, the pesticide molecule follows the same events as it does in an inert atmosphere excepting that the fragments of the pesticide produced do not react with each other (cf. Chopra, 1972). There is a mathematical reason to it. For instance, the probability of the formation of tetrachloroethylene from the dimerization of dichlorobenzene in the smoke of tobacco treated with 20 ppm endosulfan I (mole concentration, $20/407 \times 10^{-6}$) will be of the order of $(20/407 \times 10^{-6})^2$ or 2.5×10^{-15} ; that is, if every endosulfan I molecule was to fragment to give dichlorocarbene. Under actual smoking conditions very few of endosulfan I molecules would be expected to yield dichlorocarbene, since that compound is quite volatile.

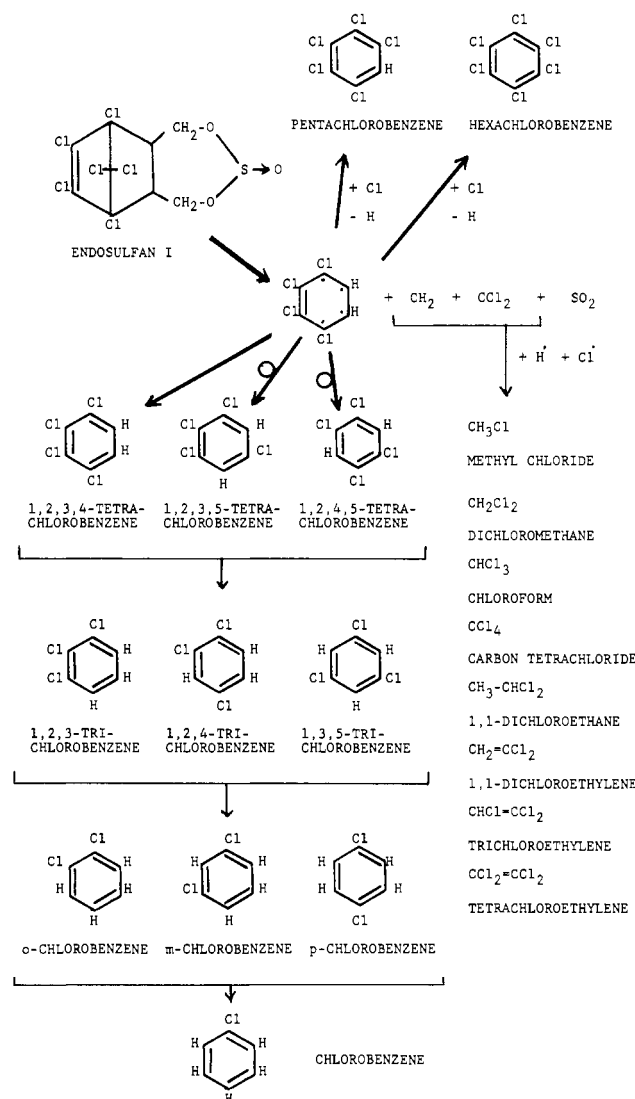


Figure 6. Mechanisms for the formation of various chlorobenzenes and chlorohydrocarbons containing one or two carbon atoms.

Besides, dichlorocarbene would be expected to survive for a very short time since it would react with water, atomic hydrogen, and other very reactive species present in the smoke. These reasons also preclude the formation of the other chlorohydrocarbons unless there is an alternate route available for their formations. Methyl chloride is formed in large quantities in tobacco smoke by the action of

methyl free radicals with inorganic chlorine (Chopra and Sherman, 1972).

Though chloroform may not be formed in the smoke of endosulfan I treated tobacco via the dichlorocarbene plus HCl route, there exists the possibility of its formation via an alternate route. 1,2,3,4,7,7-Hexachloronornbornadienes when heated to 220 to 270 °C give trichloromethylbenzenes (Molotsky, 1960). A similar event could be expected to occur during the pyrolysis of endosulfan I in tobacco smoke. The trichloromethyl group so formed could breakaway from the rest of the molecule to give a CCl₃ free radical, which in turn could react with atomic hydrogen to give chloroform (cf. Chopra and Sherman, 1972). We smoked tobacco containing 570 ppm endosulfan I but were unable to detect any chloroform (Chopra and Campbell, 1977), although we were able to detect chloroform in 2.4 ppm *p,p'*-DDT treated tobacco smoke (Chopra and Sherman, 1972). Thus, we conclude that at such high temperatures (880–900 °C) the dichloromethano bridge of endosulfan preferentially fragments into dichlorocarbene.

Thus, the endosulfan I breakdown products which may have a *mathematical* chance of being produced in endosulfan-treated tobacco smoke are: endosulfan I and II, endosulfan sulfate (formed by the oxidation of endosulfan I and II), endosulfan ether, endosulfan lactone (formed by the oxidation of endosulfan ether), hexachlorocyclopentadiene, mono-, di-, tri-, and tetrachlorobenzenes.

In pyrolysis, temperature and time are very important factors. More volatile compounds in tobacco largely escape the destructive effects of heat (Chopra and Thekkekan-dam, 1973). It can be reasonably expected that several of these compounds, which have a mathematical possibility of formation, may not be formed during the smoking of endosulfan treated tobacco since endosulfan I is quite volatile under these conditions.

We are planning to report the presence of endosulfan degradation products in endosulfan-treated tobacco smoke at some later date.

SUMMARY

With the objective of studying the possible degradation products of endosulfan in endosulfan-treated tobacco smoke, endosulfan I was pyrolyzed at 880–900 °C in a nitrogen atmosphere. Four types of compounds were identified in the pyrolysate: (1) endosulfan II, an endosulfan I rearrangement product; (2) endosulfan ether, formed by the elimination of SO₂ from endosulfan I; (3) hexachlorocyclopentadiene, a reverse Diels-Alder product; and (4) all chlorobenzenes and chlorohydrocarbons con-

taining one or two carbon atoms; such as, methyl chloride, dichloromethane, chloroform, carbon tetrachloride, 1,1-dichloroethylene, 1,1-dichloroethane, trichloroethylene, and tetrachloroethylene all of which were formed from the fragments produced by the endosulfan I cycloelimination reactions. From the reaction mechanisms involved in the formation of these compounds it is postulated that the endosulfan degradation products, which have a mathematical chance of being present in tobacco and cigarette smokes are: endosulfan I and II, endosulfan sulfate, endosulfan ether, endosulfan lactone, mono-, di-, tri-, and tetrachlorobenzenes, and hexachlorocyclopentadienes.

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