A Mechanistic Study on the Formation of the Non-Volatile Degradation Products of p,p'-DDT and p,p'-TDE in p,p'-DDT- and p,p'-TDE-Treated Tobacco Smoke*

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This paper is the last of our series "Systematic studies on the breakdown of p,p'-DDT in tobacco smokes" (3, 4, 5, and 6). In the earlier papers we have described our work and findings on: [1] the mechanisms of the breakdown of p,p'-DDT in a nitrogen atmosphere (3, 5); [2] the isolation and identification of the non-volatile degradation products of p,p'-DDT in p,p'-DDT-treated tobacco smoke, such as p,p'-DDT [2,2-di-(p-chlorophenyl)-1,1,1-trichloroethane], p,p'-DDE [2,2-di-(p-chlorophenyl)-1,1-dichloroethylene], p,p'-TDE [2,2-di-(p-chlorophenyl)-1,1-dichloroethane], p,p'-DDM [2,2-di-(p-chlorophenyl)-1-chloroethylene], trans-DCS [trans-4,4'-dichlorostilbene], DCBP [4,4'-dichlorobenzophenone], BCPM [bis-(p-chlorophenyl)-methane] (3, 4); and [3] the identification and estimation of the volatile degradation products of p,p'-DDT in p,p'-DDT-treated tobacco smoke (6).

In the present study we have quantitatively estimated the non-volatile degradation products of p,p'-DDT in p,p'-DDT-treated tobacco smoke with a view of finding the mechanisms of pesticide breakdown during the smoking of tobacco. To give it a broader scope we have also included p,p'-TDE in the study. Even though this study does not quantitatively represent the breakdown of p,p'-DDT or p,p'-TDE in cigarette smokes, it is the first study reported on the breakdown of DDT in tobacco smoke. (No such study has been reported on the breakdown of TDE in cigarette smokes either.) Hoffmann et al. (7) and Nesemann and his co-workers (8) have found DDT, TDE and other chlorinated hydrocarbons in cigarette smokes, but it is not valid to say that these compounds were DDT degradation products because these workers used cigarettes in which the tobacco contained DDT, TDE, DDE, DDM and even lindane. Bowery et al. (1) have studied the breakdown of TDE in cigarette smokes. But they have reported only the presence of TDE and DDM (TDEE) in cigarette main-stream smoke. Thus, as far as the breakdown of TDE in cigarette smokes is concerned, their study is still incomplete. The importance of our study lies in that it sheds some light into the mechanisms of the breakdown of pesticides in tobacco smoke, which the studies by other workers failed to do.

EXPERIMENTAL AND RESULTS

Materials

All solvents used were of "pure" grade and were distilled before use. ("Pure" grade refers to the quality of the reagent as mentioned on the reagent bottles.) p,p'-DDT and p,p'-TDE were 99.9% pure. All reference compounds were purified wherever necessary to give one peak in the GLC. Pesticide-free tobacco was obtained from North Carolina State University, Raleigh, and activated Florisil and deactivated alumina were prepared according to Chopra and Domanski (3).

Preparation of Tobacco Samples

Tobacco samples were humidified to 12% moisture content and then fortified with p,p'-DDT and p,p'-TDE hexane solutions to give tobacco samples containing 20 ppm p,p'-DDT, 200 ppm p,p'-DDT, 20 ppm p,p'-TDE, and 200 ppm p,p'-TDE.

Smoking of Tobacco Samples

The untreated and treated tobacco samples (10 g) were smoked in a vycor tube (2.5 cm diam. $\times$ 12.5 cm) (see Figure 1) by igniting the tobacco at the top and then drawing enough air (1.5 litres/min.) to make the smoking self-sustaining. The smoke was collected in a train consisting of eight traps, and two Cambridge filters [also see Chopra and Domanski (3)]. The smoke condensates in the traps and on the Cambridge filters were extracted with pentane and the extracts processed as shown in Figure 2. In this process all the chlorohydrocarbons in the tobacco smoke condensates got concentrated in the concentrate "H".

Estimations of p,p'-DDT and p,p'-TDE and their Degradation Products

Recovery curves for various pesticides were prepared by spiking smoke condensates from 1 g of untreated tobacco with appropriate amount of the chlorohydrocarbon and then estimating the amount of chlorohydrocarbon present in their concentrates "H", by GLC. For p,p'-DDT, p,p'-TDE, and p,p'-DDE a 6 ft. $\times$ 1/4" diam. 3% SE 30 on Chromport XXX column with an E. C. detector was used, and for the others, i. e. p,p'-DDM, BCPM, DCBP, and trans-DCS, a 6 ft. $\times$ 1/4" diam. 3%

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Figure 1. Apparatus for smoking tobacco.

OV-1 on Chromsorb W column with a Coulson Electrolytic Conductivity detector was used. The recoveries for various chlorohydrocarbons ranged between 85–105%.

Tobacco samples containing 20 ppm and 200 ppm of *p,p'*-DDT and *p,p'*-TDE were smoked and processed as mentioned above. The amounts of *p,p'*-DDT and *p,p'*-TDE and their degradation products are shown in Table 1. In Table 2 are shown the percentage conversions of *p,p'*-DDT and *p,p'*-TDE into various degradation products.

Figure 2. Clean-up procedure for the tobacco smoke condensates.

Table 1. Amounts of p,p'-DDT and p,p'-TDE, and their degradation products present in smoke condensates from 10 g of 20 ppm p,p'-DDT-, 200 ppm p,p'-DDT-, 20 ppm p,p'-TDE- and 200 ppm p,p'-TDE-treated tobacco smoke.

Compound	Tobacco samples containing			
	20 ppm p,p'-DDT	200 ppm p,p'-DDT	20 ppm p,p'-TDE	200 ppm p,p'-TDE
p,p'-DDT	0.007 mg 0.006	0.052 mg 0.060	— —	— —
p,p'-TDE	0.014 0.011	0.078 0.084	0.131 mg 0.124	1.07 mg 1.09
p,p'-DDE	0.105 0.091	0.236 0.235	0.004 0.005	0.002 0.003
p,p'-DDM	0.020 0.024	0.427 0.433	0.036 0.043	0.613 0.710
DCBP	Trace Trace	0.008 0.010	— —	Trace Trace
Trans-DCS	— —	— —	Trace Trace	Trace Trace
BCPM	0.005 0.006	0.028 0.025	— —	0.004 0.004

Table 2. Percentage of p,p'-DDT and p,p'-TDE converted into their degradation products during the smoking of tobacco samples treated with 20 ppm p,p'-DDT, 200 ppm p,p'-DDT, 20 ppm p,p'-TDE, and 200 ppm p,p'-TDE.

Degradation products	Percentage of p,p'-DDT converted into its degradation products in tobacco samples treated with		Percentage of p,p'-TDE converted into its degradation products in tobacco samples treated with	
	20 ppm p,p'-DDT	200 ppm p,p'-DDT	20 ppm p,p'-TDE	200 ppm p,p'-TDE
p,p'-DDT	3.20	2.80	—	—
p,p'-TDE	6.80	4.48	63.75	54.00
p,p'-DDE	54.67	13.18	2.22	0.14
p,p'-DDM	13.64	26.84	22.35	37.30
DCBP	Trace	0.61	—	Trace
Trans-DCS	—	—	Trace	Trace
BCPM	3.91	1.96	—	0.26
Total	82.22	49.87	88.32	91.70

DISCUSSIONS AND CONCLUSIONS

The results obtained in this study are interesting in more than one way: [1] They support the mechanism of smoking process as proposed by the senior author (2) according to which as the burning zone ABCD approaches the point "W" in the Figure 3, the pesticide molecule at that point first comes in contact with gases which are not too hot. If the molecule, under those conditions, is volatile enough, it escapes destruction. Thus of 20 ppm and 200 ppm p,p'-DDT-treated tobacco only 3.20% and 2.80% of p,p'-DDT escapes

in tobacco smoke, while the corresponding values for the more volatile p,p'-TDE are 63.75% and 54.00%. [2] The above-mentioned values also show that when the concentration of pesticide is high a greater percentage of the pesticide is destroyed than when it is low. [3] Smoking is a very short-timed pyrolysis reaction. Assuming the width of the burning zone to be 2 mm, it would take a molecule about 0.04 seconds to pass through the burning zone. (The value for a cigarette would be 0.03 seconds.) After it has passed through the burning zone the temperature of the molecule falls rapidly and soon it becomes rather inactive. An example of this is trans-DCS. According to Chopra et al. (4) the precursor of trans-DCS is p,p'-DDM. Its formation is shown below:

and p,p'-DDM can be formed from p,p'-DDT and p,p'-TDE as follows:

Figure 3. Temperature profile of a smoking cigarette.

Thus *p,p'*-DDT is three steps away from *p,p'*-DDM, while *p,p'*-TDE is just next to *p,p'*-DDM. Consequently, *p,p'*-DDT should give less DCS than even the more volatile *p,p'*-TDE. This is actually borne out experimentally. We were not able to detect any trans-DCS in *p,p'*-DDT-treated tobacco smoke condensates, while those of *p,p'*-TDE-treated tobacco smoke did show traces of trans-DCS. We would, therefore, suggest that the trans-DCS which Hoffmann and Rathkamp (7) reported to be present in cigarette smokes actually came from *p,p'*-DDM present in cigarette tobacco and not from *p,p'*-DDT present in it. Thus, time factor being of a great importance the "primary", "secondary", and "tertiary" reactions take place in the order given. [4] During the pyrolysis weaker bonds are broken first: thus the formation of BCPM would indicate that C₁-C₂ bond in DDT and TDE breaks rather easily, and the dichlorodiphenylmethyl radical so formed can pick up a hydrogen atom to give BCPM. In contrast, the formation of DCBP would require the rupture of C₁-C₂ and C₂-H bonds, or C₁=C₂ bond, if the DCBP is formed from *p,p'*-DDE or *p,p'*-DDM. These would, obviously, require more energy. Therefore, it does not take place so readily. [5] The formation of *p,p'*-DDE in *p,p'*-TDE-treated tobacco smoke indicates that the *p,p'*-TDE molecule can lose HCl to give *p,p'*-DDM or 2H to give *p,p'*-DDE.

SUMMARY

Tobacco samples containing 20 ppm *p,p'*-DDT, 200 ppm *p,p'*-DDT, 20 ppm *p,p'*-TDE and 200 ppm *p,p'*-TDE were smoked and their smoke condensates analyzed for the *p,p'*-DDT and *p,p'*-TDE degradation products such as *p,p'*-DDT, *p,p'*-TDE, *p,p'*-DDE, *p,p'*-DDM, trans-dichlorostilbene, bis-(*p*-chlorophenyl)methane, and *p,p'*-dichlorobenzophenone. The degradation patterns

and the amounts in which these degradation products were present in smoke condensates showed that 1. during the smoking process the more volatile compound has a better chance of not being destroyed; 2. the higher the amount of pesticide present in tobacco, the greater is the percentage loss of pesticide on smoking; 3. smoking being a pyrolytic reaction of a very short duration, "primary", "secondary", and "tertiary" reactions take place in the order given; 4. reactions, which have lesser energy requirements, occur more readily than those which have a higher requirement; 5. in the case of *p,p'*-TDE-treated tobacco smoke, some *p,p'*-DDE is also formed by the dehydrogenation of *p,p'*-TDE.

ZUSAMMENFASSUNG

Tabakproben, die jeweils 20 ppm bzw. 200 ppm *p,p'*-DDT und 20 ppm bzw. 200 ppm *p,p'*-TDE enthielten, wurden verraucht. Die Rauchkondensate wurden auf ihren Gehalt an *p,p'*-DDT- und *p,p'*-TDE-Abbauprodukten, wie *p,p'*-DDT, *p,p'*-TDE, *p,p'*-DDE, *p,p'*-DDM, trans-Dichlorstilben, Bis-(*p*-chlorphenyl)methan und *p,p'*-Dichlorbenzophenon, untersucht. Die Abbaumechanismen und die Mengen der im Rauchkondensat nachgewiesenen Abbauprodukte zeigten folgendes: 1. Für leichter flüchtige Verbindungen ist die Wahrscheinlichkeit größer, während des Rauchvorganges nicht zerstört zu werden. 2. Je größer die im Tabak befindliche Pestizidmenge ist, desto größer ist während des Rauchens prozentual deren Abnahme. 3. Da Rauchen eine pyrolytische Reaktion von sehr kurzer Dauer darstellt, laufen „primäre“, „sekundäre“ und „tertiäre“ Reaktionen in der angeführten Reihenfolge ab. 4. Reaktionen, die weniger Energie brauchen, laufen leichter ab als solche mit größerem Energiebedarf. 5. In dem Rauch von Tabak, der mit *p,p'*-TDE behandelt worden ist, bildet sich auch *p,p'*-DDE durch Dehydrierung von *p,p'*-TDE.

RESUME

On a fumé des échantillons de tabac contenant 20 ppm et 200 ppm de *p,p'*-DDT et 20 ppm et 200 ppm de *p,p'*-TDE, et l'on a analysé les produits de dégradation du *p,p'*-DDT et du *p,p'*-TDE dans le condensat de fumée: *p,p'*-DDT, *p,p'*-TDE, *p,p'*-DDE et *p,p'*-DDM, le trans-dichlorostilbène, le bis-(*p*-chlorophényl)méthane et le *p,p'*-dichlorobenzophénone. Les mécanismes de dégradation et les teneurs en produits de dégradation dans les condensats de fumée ont montré que: 1) pendant le processus de fumage, le composé le plus volatil a le plus de chances de ne pas être détruit; 2) le pourcentage de perte de pesticide pendant le fumage est d'autant plus important que la teneur en pesticide dans le tabac est plus haute; 3) le processus de fumer étant une réaction pyrolytique de très courte durée, des réactions se passent dans l'ordre suivant: «primaires», «secondaires», «tertiaires»; 4) les réactions requérant moins d'énergie se font plus rapidement que celles en

exigeant plus; 5) dans le cas de la fumée de tabac traité au p,p'-TDE, il se forme un peu de p,p'-DDE par déhydrogénation du p,p'-TDE.

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