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Regioselectivity of Dechlorination of DDT and its Metabolites in Mass Spectrometry

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DDT and several of its metabolites were synthesized with their aromatic chlorines enriched with ^{37}Cl. The mass spectra of these compounds were recorded under electron impact and under methane positive-ion and electron-capture negative-ion chemical ionization. The regioselectivity of the dechlorination reactions was determined by measurement of the relative proportions of the unlabeled aliphatic versus the labeled aromatic chlorines in the various fragment ions observed. For all the α,β-unsaturated compounds studied under electron impact ionization, the regioselectivity is small, as both the aromatic and the aliphatic chlorines are lost. Under positive-ion chemical ionization, the dechlorination is highly regioselective, the aliphatic chlorines being almost exclusively lost. Under electron-capture negative-ion chemical ionization, the regioselectivity is also very high and the reactivity of the various chlorines is often controlled by the position of the aromatic chlorines.

INTRODUCTION

The widespread use of the pesticide 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane (DDT) has led to worldwide contamination of the food chain. This chemical and its metabolites, 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (DDE), 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDD) and 2,2-bis(4-chlorophenyl)chloroethylene (DDMU), are still found in many food products. Analysis of these residues by gas chromatography/mass spectrometry (GC/MS), especially under chemical ionization conditions, has been proposed as a useful and sensitive method of identification.[1,2]

As is the case with many other chlorinated aromatics under various ionization conditions, the mass spectra of DDT and its metabolites show series of ions corresponding to successive loss of chlorine from the molecular ion.[1–4] Many publications have dealt with the mechanisms of these reactions, especially with respect to the position of the aromatic chlorines.[1–4] While both aromatic chlorines of DDT are *para*-substituted with respect to the α-carbon, commercial DDT preparations always contain various amounts of the *o,p'*-isomer. Therefore, *o,p'*-DDT metabolites are also found in the environment. In order to study the regioselectivity of the dechlorination reactions of *p,p'*- and of *o,p'*-DDT and their metabolites, we synthesized these compounds with the aromatic chlorines labeled with ^{37}Cl and recorded their mass spectra under electron impact (EI) and methane positive-ion (CI) and electron-capture negative-ion chemical ionization (ECNCI). This work was performed as part of a continuing study of the dechlorination reactions of chlorinated organic compounds.[5,6]

EXPERIMENTAL

Chemicals

Organic compounds were purchased from Aldrich (Milwaukee, WI, USA). $Na^{37}Cl$ (isotopic purity 94.97%) was obtained from Isotech (Miamisburg, OH, USA).

Synthesis

The synthetic pathway used to generate the various DDT metabolites is presented in Fig. 1. Syntheses of DDT and its metabolites were first performed with unlabeled chlorobenzene and the purity and identity of the products were determined by comparison with authentic standards using GC/MS. Typically, 0.62 ml of aniline (6.8 mmol) was diazotized with 0.480 g of sodium nitrite (6.9 mmol) in 6.0 ml of a solution containing 4.0 ml of 20% sulfuric acid and 2.0 ml of acetonitrile. To this solution was added 0.612 g of $Cu^{37}Cl$ (6.1 mmol), made from $Na^{37}Cl$,[7] and the mixture was stirred overnight. After work-up, the organic residue was purified by silica flash chromatography (Kieselgel 60, Merck, Darmstadt, Germany), using pentane as eluent, to give 0.585 g of ^{37}Cl-labeled chlorobenzene. This compound was then reacted with 0.10 g of trichloroacetaldehyde in 1.0 ml of sulfuric acid at 4 °C overnight. The organic residue was purified by silica

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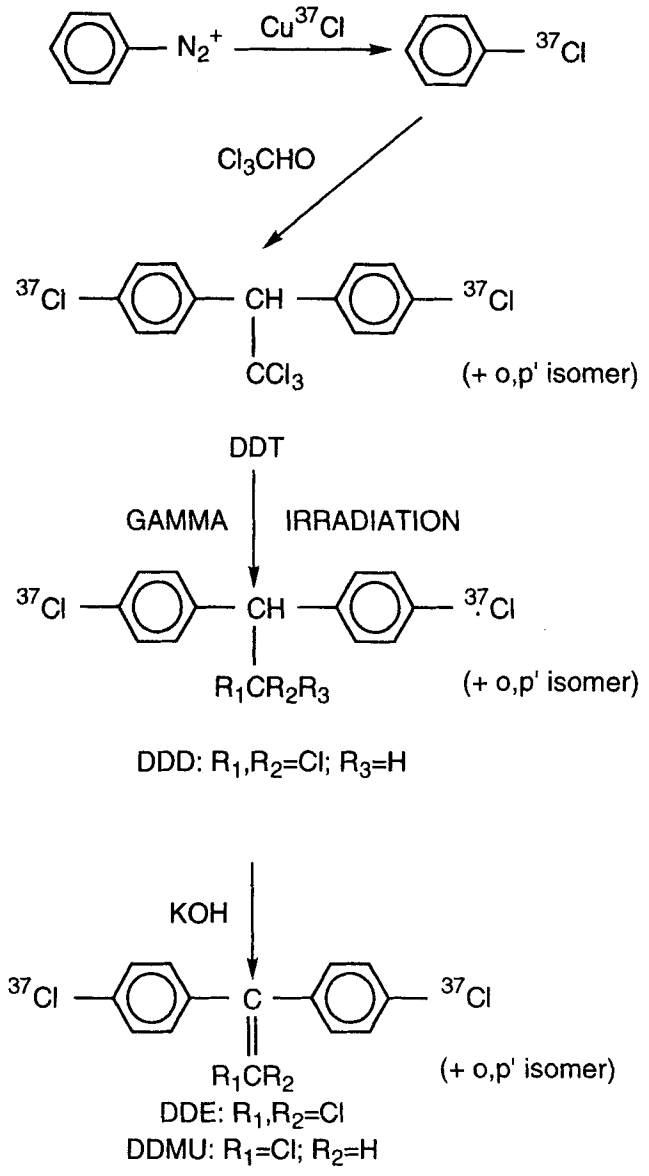

Figure 1. Synthetic pathways of ^{37}Cl-labeled DDT and its metabolites.

thick-layer chromatography (Kieselgel 60, 1 mm thickness, Merck), using pentane as eluent, to give 103 mg of *p,p'*-DDT and 15 mg of *o,p'*-DDT.

In order to obtain the lower chlorinated analogs of DDT, dechlorination of the trichloromethyl function with zinc under various conditions was attempted without success, the completely dechlorinated analogs being preferentially produced. Because gamma irradiation of DDT in propan-2-ol generates the monodechlorinated intermediates in good proportions,[8] several dechlorinated compounds known to be DDT metabolites were produced by gamma irradiation at 40 kGy of 170 ppm solutions of *p,p'*- and *o,p'*-DDT in propan-2-ol. The corresponding *p,p'*- and *o,p'*-DDE and -DDMU were obtained by treating these propan-2-ol solutions with KOH at a final concentration of 0.8 M for 20 min at 50 °C. Because there is a moderate amount of unreacted starting material left after irradiation, these compounds were obtained as mixtures. As all these compounds can easily be separated by GC, their isolation was not attempted and the propan-2-ol solutions were mixed in various proportions in order that similar total ion abundances were obtained for each compound in GC/MS. A total ion chromatogram of the mixture is presented in Fig. 2.

Mass spectrometry

Identification of the various labeled DDT metabolites was performed using a Finnigan ITD 800 ion trap coupled to a Varian Model 3500 chromatograph equipped with a 30 m × 0.3 mm i.d. DB-5 column (J and W Scientific), film thickness 0.25 μm, with helium as carrier gas. The column temperature was initially set at 100 °C, increased to 220 °C at 20 °C min^{-1}, to 260 °C at 2 °C min^{-1} and to 310 °C at 20 °C min^{-1}. The injector temperature was 250 °C. The $^{35}Cl/^{37}Cl$ ratios in the fragment ions of DDT and its metabolites were determined under EI, CI and ECNCI conditions using a Hewlett–Packard Model 5988A quadrupole analyzer coupled to a Hewlett–Packard 5890 gas chromatograph, with a capillary column and a temperature program similar to those described above. The source temperature was 150 °C. Methane, at a pressure of 0.3 Torr (1 Torr = 133.3 Pa), was used as the reagent gas in positive-ion CI mode and as moderator in the ECNCI mode. The scan range was *m/z* 70–400. Analyses were performed in triplicate.

Isotopic analysis

In a first step, the ^{37}Cl enrichment of the aromatic chlorines of DDT was determined by analysis of the $^{35}Cl/^{37}Cl$ ratios of the abundant *m/z* 235-239 ion clusters in the EI spectra of the various α,β-unsaturated DDT metabolites using a previously described method.[5] This ion cluster corresponds to the bis(chlorophenyl)methyl cation and is thus ideal for calculation of the ^{37}Cl enrichment of the aromatic chlorines of the labeled DDT, assuming that under EI conditions no significant chlorine scrambling occurs. The calculated ^{37}Cl enrichment of the aromatic chlorines of DDT was 94.6%, a value in agreement with the isotopic purity of the $Na^{37}Cl$.

The averaged mass spectrum of each of the chromatographic peaks of interest in Fig. 2 was analyzed for each of the ion clusters corresponding to the loss of one, two or three chlorines from the molecular ion. The abundances of each of the three most abundant ions in a given cluster were corrected for ^{13}C content in lighter ions and were then divided by the abundance of the most abundant ion of that cluster. These two relative abundances were then averaged with the other two sets of data, as these analyses were performed in triplicate set. In order to evaluate the reproducibility of the measurements within each triplicate set, the maximum error of each measurement with respect to the mean was calculated. For all the measurements, this value averaged 3.4% and never exceeded 6.0%.

A series of clusters were then generated mathematically. For each of these clusters, the relative abundances of all isotopic ions were calculated using equations of

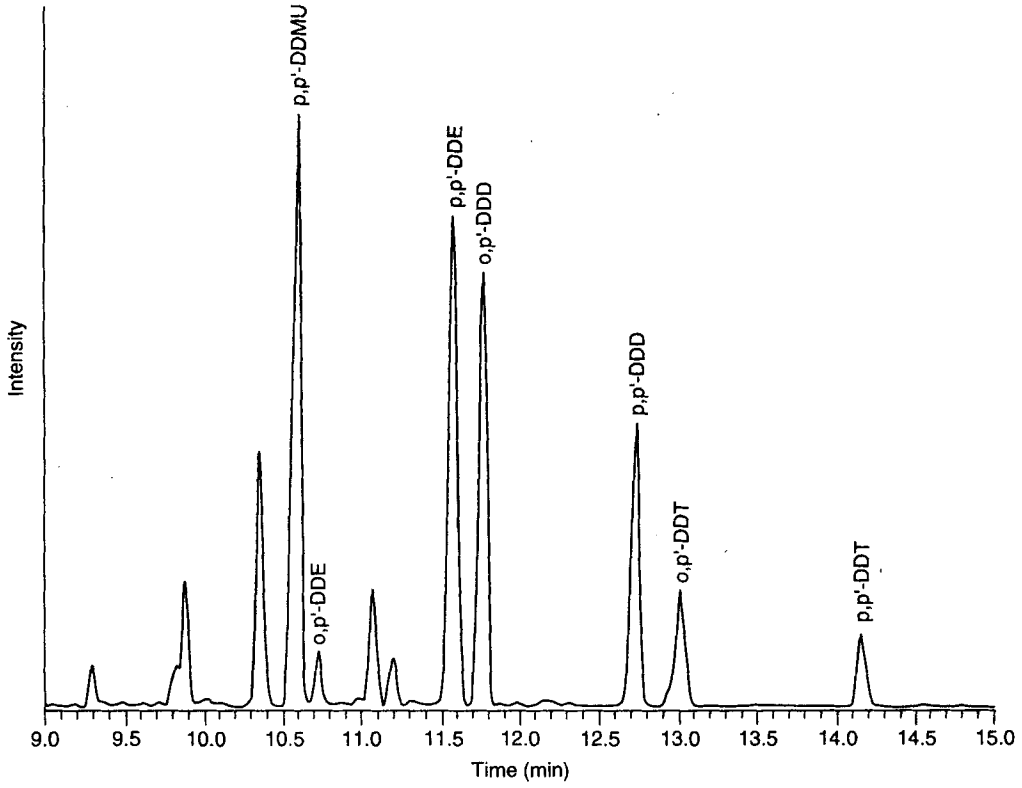

Figure 2. EI total ion chromatogram of the various labeled DDT metabolites synthesized and mixed as described in the text.

the type $(a + b)^n \times (A + B)^m$, where $(a + b)$ and $(A + B)$ represents the relative proportions of ^{35}Cl and ^{37}Cl in the aliphatic and aromatic chlorines, respectively. The values of n and m represent the different possible numbers of aliphatic and aromatic chlorines, respectively, in the fragment ion of interest. For the aliphatic chlorines, which were derived from trichloroacetaldehyde, the a and b values are those of the natural isotopic abundances of chlorine. For the aromatic chlorines, the values of A and B are 5.4% and 94.6%, respectively, as obtained from the m/z 235–239 ion cluster of DDT in EI as described previously.

The m/z 246 ion cluster of DDE as observed in EI will be used here for a sample calculation. This cluster represents the loss of two chlorines from the molecular ion. This fragment thus contains the two remaining chlorines, and hence $m + n = 2$. There are three possibilities: $m = 2$ and $n = 0$, $m = 1$ and $n = 1$, and $m = 0$ and $n = 2$. With these values, three different series of relative ion abundances can be calculated. They can be treated as three simultaneous linear equations to be solved for the three largest ion abundances observed. This was performed by matrix inversion by the Gauss elimination method, using a program written in BASIC.[9] The uncertainty in the calculated values was determined by propagation of error to be 6% for the set of measurements in triplicate that had the largest deviation in the mean (6%). In some instances, when two ion clusters overlapped by 2 u, as for example the ions at m/z 246 [M − H − 3Cl] and 248 [M + H − 3Cl] in the ECNCI spectrum of *o,p'*-DDT, the relative total abundances of the two clusters have to be obtained from the corresponding unlabeled compounds prior to calculations with the labeled analog.

Because the isotopic analysis of a given ion cluster was performed by measurement of the relative abundances of the three most abundant ions of each cluster, the aliphatic/aromatic chlorine content of clusters which were not sufficiently abundant could not be reliably calculated. To simplify annotation, the mass assignment of ion clusters will be described in the following sections as if they were generated from unlabeled compounds.

RESULTS

Electron impact

Table 1 presents the relative aliphatic and aromatic chlorine contents of ions undergoing dechlorination under EI conditions for a series of DDT metabolites. Only the metabolites which contain a double bond between the α- and β-carbons show ions arising from successive losses of chlorine. The most abundant ions of these metabolites are those of the molecular ion and of ions corresponding to subsequent loss of two chlorine atoms. Lower abundance ions corresponding to loss of Cl and HCl from the molecular ion were also observed.

DDT and its α,β-saturated metabolites undergo cleavage of this carbon–carbon bond and, accordingly, their mass spectra consist almost exclusively of an m/z 235–239 ion cluster, independent of the position of the aromatic chlorines. This is due to the great stability of this cation, which probably has the structure of a phenyl-substituted tropylium ion.[10] The profiles of the

Table 1. Proportions of aliphatic and aromatic chlorines in electron impact fragment ions of DDT metabolites

Compound	Fragment ions (*m/z*)[a]	Cl substitution in ion (aliphatic:aromatic)	Relative proportion[b]
p,p'-DDE (2:2)[c]	281 [M − Cl]	1:2	66
		2:1	34
	280 [M − HCl]	1:2	72
		2:1	28
	246 [M − 2Cl]	0:2	41
		1:1	49
		2:0	9
o,p'-DDE (2:2)	246 [M − 2Cl]	0:2	12
		1:1	69
		2:0	18
p,p'-DDMU (1:2)	247 [M − Cl]	0:2	95
		1:1	5
	246 [M − HCl]	0:2	81
		1:1	19
	212 [M − 2Cl]	0:1	79
		1:0	21

[a] The chlorine loss is presented relative to the molecular ion in a cumulative sense. This does not infer necessarily that the molecular ion is the parent ion.
[b] These values are the percentages of the total ion cluster abundance corresponding to the aliphatic/aromatic chlorine ratios given in the third column.
[c] Numbers in parentheses are the number of aliphatic:aromatic chlorines in the molecular ion.

m/z 235–239 ion clusters of these metabolites were used to calculate the ^{37}Cl enrichment of the aromatic chlorines.

For *p,p'*-DDE, two low-abundance ion clusters corresponding to losses of Cl and of HCl appear at *m/z* 281 and 280, respectively. If the chlorine loss reaction was random, the ion current arising from the loss of an aliphatic chlorine should be the same as that arising from the loss of an aromatic chlorine, as they are present in equal amounts in the molecule. The *m/z* 281 and 280 clusters are enriched in ^{37}Cl over what would be expected if the chlorine loss was random. This is indicative that aliphatic chlorine is preferentially lost and that dechlorination is partially regioselective, as a substantial amount of aromatic chlorine is also lost. The more abundant ion cluster at *m/z* 246 (loss of two chlorine atoms) also shows the same trend as, overall, more aliphatic chlorines are lost than aromatic chlorines. For the *o,p'*-DDE isomer, only the [M − 2Cl] ion cluster (*m/z* 246) was sufficiently abundant to be analyzed. The aliphatic/aromatic chlorine content of this ion shows that 69% of the ion current arises from loss of one aliphatic and one aromatic chlorine, in contrast to the *p,p'*-isomer, in which only 49% of the [M − 2Cl] cluster (*m/z* 246) is formed by loss of one of each type.

For *p,p'*-DDMU, two low-abundance clusters corresponding to losses of Cl (*m/z* 247) and of HCl (*m/z* 246), and a more abundant cluster corresponding to the loss of two chlorine atoms (*m/z* 212), were also observed. The aliphatic chlorine was much more labile than with *p,p'*- and *o,p'*-DDE for the first chlorine loss. This is surprising, as the ratio of aliphatic to aromatic chlorine in DDMU is half that for DDE. If the dechlorination reaction was proceeding randomly, the probability of losing an aliphatic versus an aromatic chlorine should be twice as large for DDE as for DDMU. The residual aliphatic/aromatic chlorine contents of the *m/z* 246 ions of *p,p'*-DDMU and *p,p'*-DDE are very different, suggesting that the ion derived from DDMU is different from that produced from *p,p'*-DDE. The [M − 2Cl] ion of *p,p'*-DDMU (*m/z* 212) contains a larger amount of aliphatic chlorine than the [M − Cl] ion (*m/z* 247), which indicates that it cannot be produced exclusively from the [M − Cl] ion and that the molecular ion is a direct precursor.

Positive-ion chemical ionization

The CI mass spectra of DDT and of its α,β-saturated metabolites present moderately abundant quasi-molecular ions and ions of greater abundance corresponding to the loss of one and two chlorines. The α,β-unsaturated analogs present abundant quasi-molecular ions and ions of lower abundance corresponding to the loss of one and two chlorines.

The aliphatic/aromatic chlorine proportions of the various ions listed in Table 2 clearly show that, under positive-ion CI conditions, chlorine loss is highly regioselective and occurs almost exclusively from the aliphatic chlorines, independently of the position of the aromatic chlorines. For the two DDT isomers, 100% of the ion current abundance can be accounted for by the loss of one or two aliphatic chlorines. For the two DDD isomers, 100% of the chlorine lost in the first dechlorination and 94% for the second dechlorination also occur from the aliphatic chlorines, independently of the position of the aromatic chlorine substitution. The

Table 2. Proportions of aliphatic and aromatic chlorines in fragment ions of DDT and its metabolites formed under positive-ion methane chemical ionization

Compound	Ion (*m/z*)[a]	Cl substitution in ion (aliphatic:aromatic)	Relative proportion[b]
p,p'-DDT (3:2)[c]	317 [MH − HCl]	2:2	100
	283 [MH − 2Cl]	1:2	100
o,p'-DDT (3:2)	317 [MH − HCl]	2:2	100
	283 [MH − 2Cl]	1:2	100
p,p'-DDD (2:2)	283 [MH − HCl]	1:2	100
	249 [MH − 2Cl]	0:2	94
		1:1	6
o,p'-DDD (2:2)	283 [MH − HCl]	1:2	100
	249 [MH − 2Cl]	0:2	94
		1:1	3
		2:0	3
p,p'-DDE (2:2)	281 [MH − HCl]	1:2	100
	247 [MH − 2Cl]	0:2	90
		1:1	10
o,p'-DDE (2:2)	281 [MH − HCl]	1:2	100
	247 [MH − 2Cl]	0:2	86
		1:1	14
p,p'-DDMU (1:2)	247 [MH − HCl]	0:2	96
		1:1	4

[a–c] See Table 1.

Table 3. Proportions of aliphatic and aromatic chlorines in fragment ions of DDT and its metabolites formed under methane electron-capture negative-ion chemical ionization

Compound	Ion (*m/z*)[a]	Type of Cl in ion (aliphatic : aromatic)	Relative proportion[b]
o,p'-DDT (3:2)[c]	246 [M − H − 3Cl]	1:1	94
		2:0	6
	247 [M − 3Cl]	2:0	100
	248 [M + H − 3Cl]	0:2	32
		2:0	68
p,p'-DDD (2:2)	248 [M − 2Cl]	0:2	95
		1:1	5
o,p'-DDD (2:2)	246 [M − 2H − 2Cl]	1:1	98
		2:0	2
	248 [M − 2Cl]	0:2	96
		2:0	4
p,p'-DDE (2:2)	280 [M − HCl]	1:2	100
	281 [M − Cl]	1:2	89
		2:1	11
	282 [M + H − Cl]	1:2	91
		2:1	9
o,p'-DDE (2:2)	246 [M − 2Cl]	0:2	3
		1:1	94
		2:0	3
p,p'-DDMU (1:2)	247 [M − Cl]	0:2	58
		1:1	42

[a–c] See Table 1.

same phenomenon also occurs for the two DDE isomers. The first dechlorination reaction of DDMU also occurs almost exclusively through loss of the single aliphatic chlorine.

Electron-capture negative-ion chemical ionization

In the ECNCI spectrum of the α,β-saturated DDT analogs (Table 3), the molecular ions and ions corresponding to the loss of one chlorine atom have a very low abundance, while those corresponding to the loss of two and three chlorines are very abundant. The unsaturated DDT analogs show abundant molecular ions and ions corresponding to the loss of one and two chlorines that are much less abundant.

p,p'-DDT showed fragment ions too weak to be usefully analyzed. The *o,p'*-isomer of DDT shows evidence of three distinct processes leading to the loss of three chlorines. The aliphatic/aromatic chlorine proportions of the *m/z* 246 ion correspond to the loss of nearly exclusively two aliphatic and one aromatic chlorine and one hydrogen with respect to the molecular ion. The *m/z* 247 ion, which corresponds to the loss of three chlorines with respect to the molecular ion, arises exclusively from the loss of two aromatic and one aliphatic chlorine. The *m/z* 248 ion, on the other hand, which corresponds to the loss of three chlorines and the addition of one hydrogen from the methane moderator gas, with respect to the molecular ion, is produced mostly through the loss of two aromatic and one aliphatic chlorine and also, to a smaller but significant extent, by loss of the three aliphatic chlorines. Since these three ions differ so much in their aliphatic/aromatic chlorines proportions, it is unlikely that they are formed by abstraction or addition of a hydrogen on the tri-dechlorinated ion, but rather that they are formed through very different mechanisms.

Both DDD isomers present [M − 2Cl] ions at *m/z* 248 which demonstrate similar extents of label loss, which indicates that these dechlorinations are not affected by the location of the aromatic chlorines. *o,p'*-DDD presents an [M − 2H − 2Cl] ion (*m/z* 246) which is not found with the *p,p'*-isomer. This fragment shows essentially the same aliphatic/aromatic chlorine proportions as the [M − 2Cl] ions (*m/z* 248) of the two DDD isomers.

p,p'-DDE shows three clusters, each corresponding to the loss of principally an aliphatic chlorine. Unfortunately, the corresponding cluster in *o,p'*-DDE was too weak to be analyzed. Only the [M − 2Cl] ion of *o,p'*-DDE (*m/z* 246) was sufficiently abundant to be studied and it contains mostly one aliphatic and one aromatic chlorine.

p,p'-DDMU shows one ion cluster corresponding to the loss of one chlorine. Its aliphatic/aromatic chlorine content shows that it is produced slightly more through the loss of one aliphatic than aromatic chlorine.

DISCUSSION

The mechanisms of dechlorination in EI of *p,p'*- and *o,p'*-DDE were studied by Safe and Hutzinger[4] using

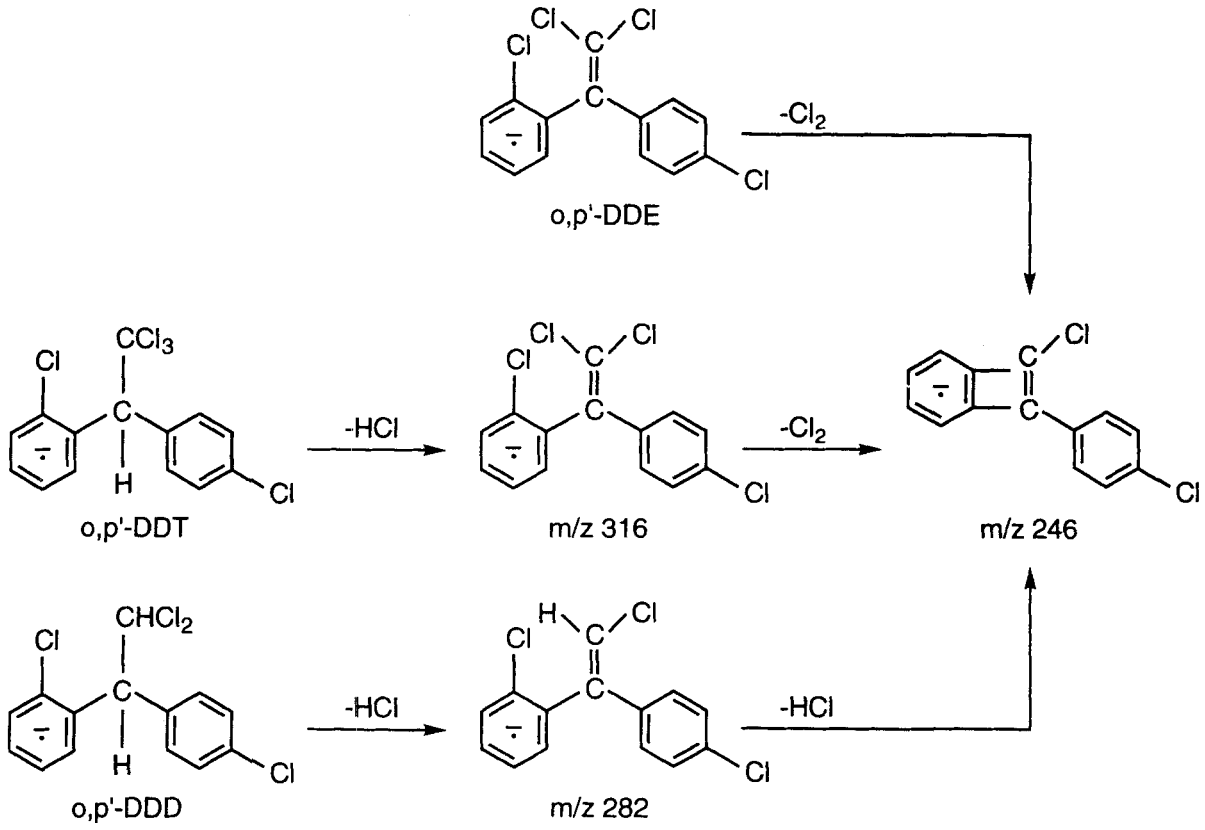

Figure 3. Formation of a cyclobutene intermediate in the dechlorination pathways of *o,p'*-DDT metabolites as proposed by Stemmler and Hites.[2]

metastable ion and ion kinetic energy (IKE) analyses. They found that the [M – Cl] ion (*m/z* 281) of *p,p'*-DDE is a precursor of the [M – 2Cl] ion (*m/z* 246). These findings are in agreement with our present data, which show that the various proportions of the aliphatic/aromatic chlorines observed in the *m/z* 246 ion can be generated by chlorine atom loss from the *m/z* 281 ion.

Sphon and Damico[3] also studied the EI dechlorination of DDE isomers. They suggested that the *m/z* 246 ion of *p,p'*-DDE is formed from the molecular ion by the loss of two chlorines through four different fragmentation pathways in equal proportions. These are the loss of two aliphatic chlorines, the loss of two aromatic chlorines and the loss of one aromatic and one aliphatic chlorine on the same and opposite sides of the double bond. In terms of aliphatic/aromatic residual content, the relative abundances of these fragments should be 1:1:2, respectively. Our results rather indicate that the aromatic chlorines are retained in preference to the aliphatic chlorines owing to the greater aliphatic chlorine reactivity, as was also observed with the *m/z* 281 precursor ion.

It was suggested in these two earlier publications,[3,4] on the basis of the IKE spectra of *p,p'*- and *o,p'*-DDE, that the [M – 2Cl] ions (*m/z* 246) of these two compounds have energetically similar structures. Our results clearly show that there is much less aromatic chlorine in the *m/z* 246 ion of *o,p'*-DDE than in the corresponding ion of the *p,p'*-isomer. A possible mechanism to explain this observation could be a facilitated formation of a four-membered ring with the second departing chlorine being the *ortho* aromatic chlorine (Fig. 3), as suggested by Stemmler and Hites[2] for the ECNCI spectra of *o,p'*-DDT metabolites.

The methane positive-ion CI spectra of the two DDT isomers show complete regioselectivity of the first and second dechlorination reactions, the aliphatic chlorine atoms being exclusively removed, independently of the position of the aromatic chlorines. Contrary to the observations of Dougherty *et al.*,[1] who used isobutane as reagent gas and reported [M – Cl] ion abundances (*m/z* 317) much larger for the *o,p'*-isomer than for the *p,p'*-isomer, we found them to have similar abundances. They attributed this large difference to stabilization of the positive charge on the *β*-carbon through the formation of a chloronium ion with the aromatic *ortho* chlorine. This implies in their model that it is an aliphatic chlorine which is lost in the formation of this ion. Even if, in our experiment, the relative abundances of the *m/z* 317 ion are similar for both DDT isomers, it is clear that it is the aliphatic chlorine which is lost, supporting the proposal of Dougherty *et al.*

The first dechlorination is also completely regioselective for the two isomers of DDD and DDE, the aliphatic chlorine also being exclusively lost. The second dechlorination is also very regiospecific, as only a very small proportion of aromatic chlorine is lost in this step. As for the two DDT isomers, the position of the aromatic chlorines has no influence on the regiospecificity of the reaction.

The dechlorination mechanisms of the various *p,p'*- and *o,p'*-DDT metabolites under methane ECNCI were studied by Stemmler and Hites.[2] They compared the

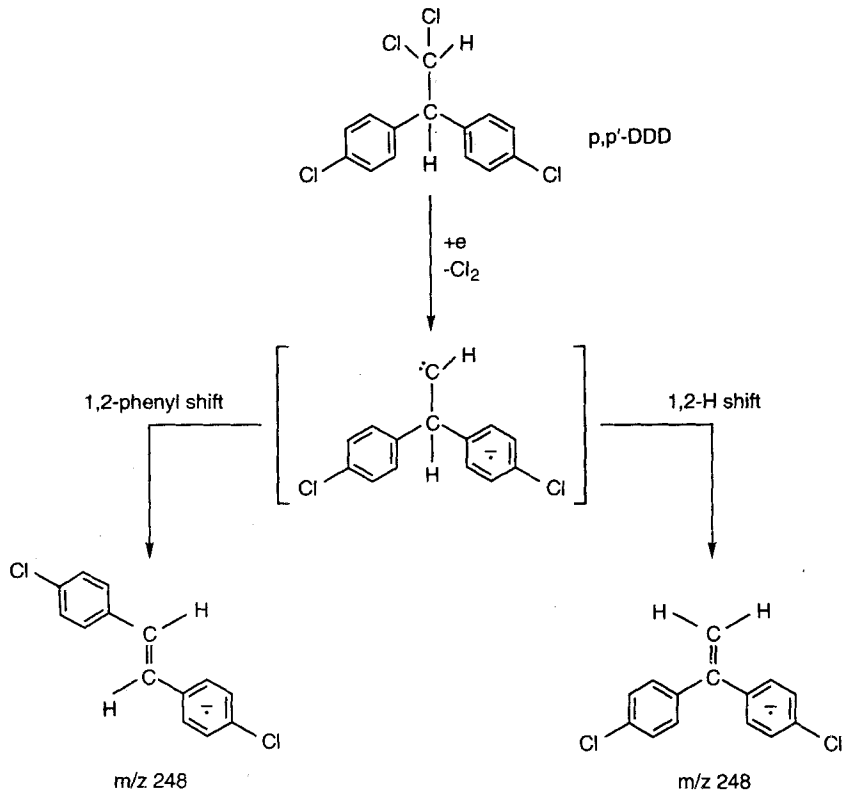

Figure 4. Formation of a carbene intermediate in the dechlorination pathway of *p,p'*-DDD as proposed by Stemmler and Hites.[2]

ECNCI spectra of these various isomers and found that the ions of many of the dechlorinated metabolites can be found in the spectra of their higher chlorinated analogs, suggesting that these less chlorinated compounds were also formed in the mass spectrometer as dechlorinated ion fragments of these higher chlorinated compounds. They attributed an abundant *m/z* 248 ion in the mass spectrum of *p,p'*-DDD to the loss of the two aliphatic chlorines from the molecular ion to produce a carbene intermediate (Fig. 4) which would rearrange to form a more stable dichlorostillbene or a bis(chlorophenyl)ethene anion. This mechanism implies that two aliphatic chlorines are lost and this is confirmed in Table 3 for the *m/z* 248 ion of *p,p'*-DDD.

Stemmler and Hites[2] also reported the ECNCI spectrum of *p,p*-DDE and found many similarities between the dechlorinated ions generated by *p,p'*-DDE and *p,p'*-DDT, suggesting that the former was a dechlorinated intermediate of *p,p'*-DDT. They also suggested that the *m/z* 281 ion of *p,p'*-DDE, which corresponds to the loss of one chlorine from the molecular ion, was also formed through the loss of one aliphatic chlorine. This is also what can be observed in Table 3, as 89% of the abundance of the *m/z* 281 ion of *p,p*-DDE comes from an ion containing only one aliphatic chlorine.

The ECNCI spectra of *o,p'*-DDT, *o,p'*-DDD and *o,p'*-DDE were also reported by Stemmler and Hites[2] to contain an abundant *m/z* 246 ion. In the present study, this ion was also very abundant for these three compounds. The structure that they proposed for this ion contained a cyclobutene ring produced by ring closure between the β-carbon and the aromatic *ortho*-carbon after the loss of the corresponding chlorines (Fig. 3). This requires that the *m/z* 246 ions for these three compounds contain only one aliphatic and one aromatic chlorine, which is in agreement with the results presented in Table 3. This strongly supports the hypothesis of Stemmler and Hites.

There are other, less abundant, ions reported in Table 3 that could be observed in the spectra presented by Stemmler and Hites[2] that they did not analyze. The masses of these ions differ by 1–2 u from the ions discussed previously, but they differ considerably from the latter ions in their relative aliphatic/aromatic chlorines proportions. This indicates that these ions are not simply produced by hydrogen abstraction from or addition to the ions discussed previously but that they are formed through different mechanisms.

CONCLUSION

Labeling of the aromatic chlorines of a series of DDT metabolites shows that dechlorination under EI is not very regioselective for the α,β-unsaturated analogs. Under less energetic conditions of CI and ECNCI, however, dechlorination becomes highly regioselective. This method of analysis is a more direct way to measure the regioselectivity of these reactions than metastable analysis or analysis of the mass spectra of the dechlorinated products. We confirm many of the proposals of other workers concerning the dechlorination mechanisms, especially under ECNCI conditions.

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