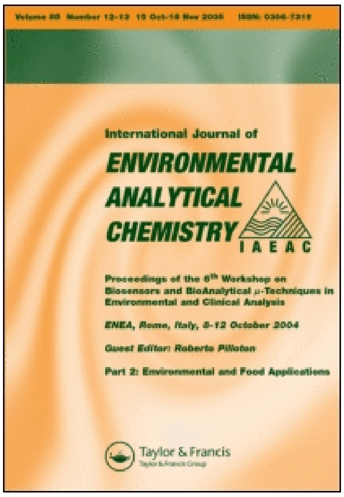

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PARTIAL DECHLORINATION OF SOME DDT INSECTICIDES AND DETERMINATION OF DDT METABOLITES IN AN ENVIRONMENTAL SAMPLE

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Partial dechlorination of a group of DDT insecticides was performed using a catalytic dechlorination technique, based on $NiCl_2/NaBH_4$ as catalyst and capillary column GC-MS. On the basis of GC-MS data obtained for the degraded DDT products, metabolites of a soil sample contaminated with DDT were identified. Furthermore, the dechlorination sequence for p, p'-DDT as proposed earlier is confirmed by GC-MS data.

KEY WORDS: DDT, dechlorination, GC-MS, Ion trap detector.

INTRODUCTION

In earlier publications we have reported on the dechlorination, detoxification and analyses of PCBs, PCNs[1]; PCDDs, PCDFs[2] and on some chlorinated cyclodiene insecticide compounds[3] using a catalytic dechlorination technique based on $NiCl_2/NaBH_4$ as the catalyst and capillary column GC-MS. In the present paper we have studied the partial dechlorination of a group of DDT insecticides to gain information on the type of metabolites that DDT may have after degradation in an environmental sample.

DDT has been an 'attractive' insecticide for many years; however, its persistence and general stability in the environment have been and remain a cause for concern. The common forms of DDT are considered to be o, p'-DDT; p, p'-DDT; o, p'-DDD and p, p'-DDD. The derivatives o, p'-DDE and p, p'-DDE may also be regarded as members of the DDT group. Furthermore, p, p'-DDT (1, 1, 1-trichloro-2,2 bis (p-chlorophenyl) ethane) and its major degradation product p, p'-DDE (1, 1-dichloro-2,2-bis (p-chlorophenyl) ethene) are now found in the environment all around the world. Quantitative analysis requires the detection of all DDT derivatives but this is difficult to achieve.

Commercial DDT consists mainly of p, p'-DDT and small amounts of o, p'-DDT; o,

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o'-DDT; and p, p'-DDE. The presence of metabolites and degradation products of some DDT compounds has been reported in the literature[4–7] but there appears to be no clear MS data on the metabolites of the DDT group of compounds[4–7] and any comparison made with an environmental sample. However, a metabolic pathway of DDT by microorganisms has been proposed.[8,9] Ballschmiter *et al.*[10] have reported a study of the DDT group of pollutants identified in fish samples from the North Atlantic and North Sea using high resolution, capillary gas chromatography with electron capture detection. In the study on the dechlorination and detoxification of PCBs and PCNs reported by the present authors[1,2] a procedure utilising $NiCl_2/NaBH_4$ and capillary column GC-MS with an ion trap detector (ITD™) was successful in the full dechlorination and analysis of these compounds to their parent compounds biphenyl and naphthalene, respectively. However, in the present work we were interested in partial dechlorination of the DDT group to identify where possible, metabolites of DDT by the MS data. We therefore, report our results on the partial dechlorination of p, p'-DDT by MS and aim to identify some of the metabolites in an environmental sample.

EXPERIMENTAL

Apparatus

A Hewlett Packard Gas Chromatograph model 5880, coupled to a Finnigan MAT ion trap detector (ITD™) and a Hewlett Packard 3880A integrator were used. GC operating conditions were, as follows: capillary column (SGE-BP1, 0.2mm × 25m) cold trapped at 65° C for 0.4 min; oven temperature ramped to 220 ° C at 20 ° C min^{-1}; injector port 250 ° C; helium gas carrier-linear velocity 30 cm^3 min^{-1}. The ITD scan mode conditions were: ionization 70 eV; transfer line at 250 ° C; 45–500 a.m.u. scan mass/charge units and 1 scan s^{-1}; injection sample 1–5 μL, splitless.

Reagents and chemicals

Reagents Sodium borohydride ($NaBH_4$, Koch-Light Laboratories, Ltd, Colnbrook, Berks, UK) and nickel chloride A.R., Ajax Chemicals, Sydney, N.S.W., Australia

Chemicals DDT, DDE, DDD and 1,1-diphenyl ethane (Foxboro Analytical, North Haven, CT 06473, USA)

Solvents Methanol, acetone, and acetonitrile were from Mallinckrodt Aust. Pty Ltd, Clayton, Victoria, Australia

Procedure

The procedure developed for the dechlorination of PCBs and PCNs, reported earlier[1], which makes use of the Ni_2B *in-situ* catalyst in conjunction with GC-MS, was used in these studies on the DDT group of compounds. It should be noted here that we were interested in partial dechlorination rather than full dechlorination which is achievable to the 1,1-diphenylethane parent compound.

RESULTS AND DISCUSSION

The dechlorination of DDT (commercial DDT containing mainly 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane); p,p'-DDT; o,p'-DDT; o,o'-DDT and p,p'-DDE was investigated. It was found that, in contrast to the PCBs and PCNs, dechlorination was most effective in methanol. In GC-MS, electron impact ionization of the DDT group appears to cause easy loss of the aliphatic portion attached to the C-2 or α-carbon (Table 1), resulting in the m/z = 235 ion. This ion forms the base peak in the p,p'-DDT spectrum. The GC profiles of partially dechlorinated p,p'-DDT are shown in Figure 1(a and b). It can be seen that the parent compound 1, 1-diphenylethane occurs at scan no. 170. This was monitored by the m/z = 167 ion corresponding to the base peak diphenyl methyl carbonium ion $[M\text{-}CH_3]^+$. The p, p'-DDT compound itself elutes, as shown, at scan no. 650. By means of GC-MS, the intermediates are identified according to the scheme proposed by Dennis and Cooper[6], as they are represented by peaks 2–7. Further, the major ion fragments for peaks 1–8 as shown in Figure 1 may be identified (Table 1) and a sequence for the dechlorination of p,p'-DDT confirms the detailed proposal by Dennis and Cooper [see ref. 6 for the proposed structures of peak 1–8].

Identification of DDT metabolites in an environmental sample

To test the potential of the degradation metabolite identified above, a soil sample known to have been contaminated with DDT was examined. The aim was to determine, whether DDT

Table 1 Characteristic Ions for Partial Dechlorination of p, p-DDT.

Scan No.	*Compound (Peak) No.*	*Major Ions† (m/z)*					
650	$C_{14}H_9Cl_5$ (1) p,p'-DDT	[235],	237,	176,	165		
530	$C_{14}H_{10}Cl_4$ (2)	[237],	165,	202,	101,	284	
386	$C_{14}H_{11}Cl_3$ (3)	[201],	167,	176			
358	$C_{14}H_{11}Cl_3$ (4)	[284],	237,	250,	212,	176	
320	$C_{14}H_{12}Cl_2$ (5)	[250],	165,	103,	201,	140	
289	$C_{14}H_{12}Cl_2$ (6)	[250],	235,	165,	103,	201,	140
236	$C_{14}H_{13}Cl_3$ (7)	[166],	201,	216,	103		
170	$C_{14}H_{14}$ (8) 1,1-diphenylethane		[167],	182			

†in order of decreasing intensity; [ ] base peak

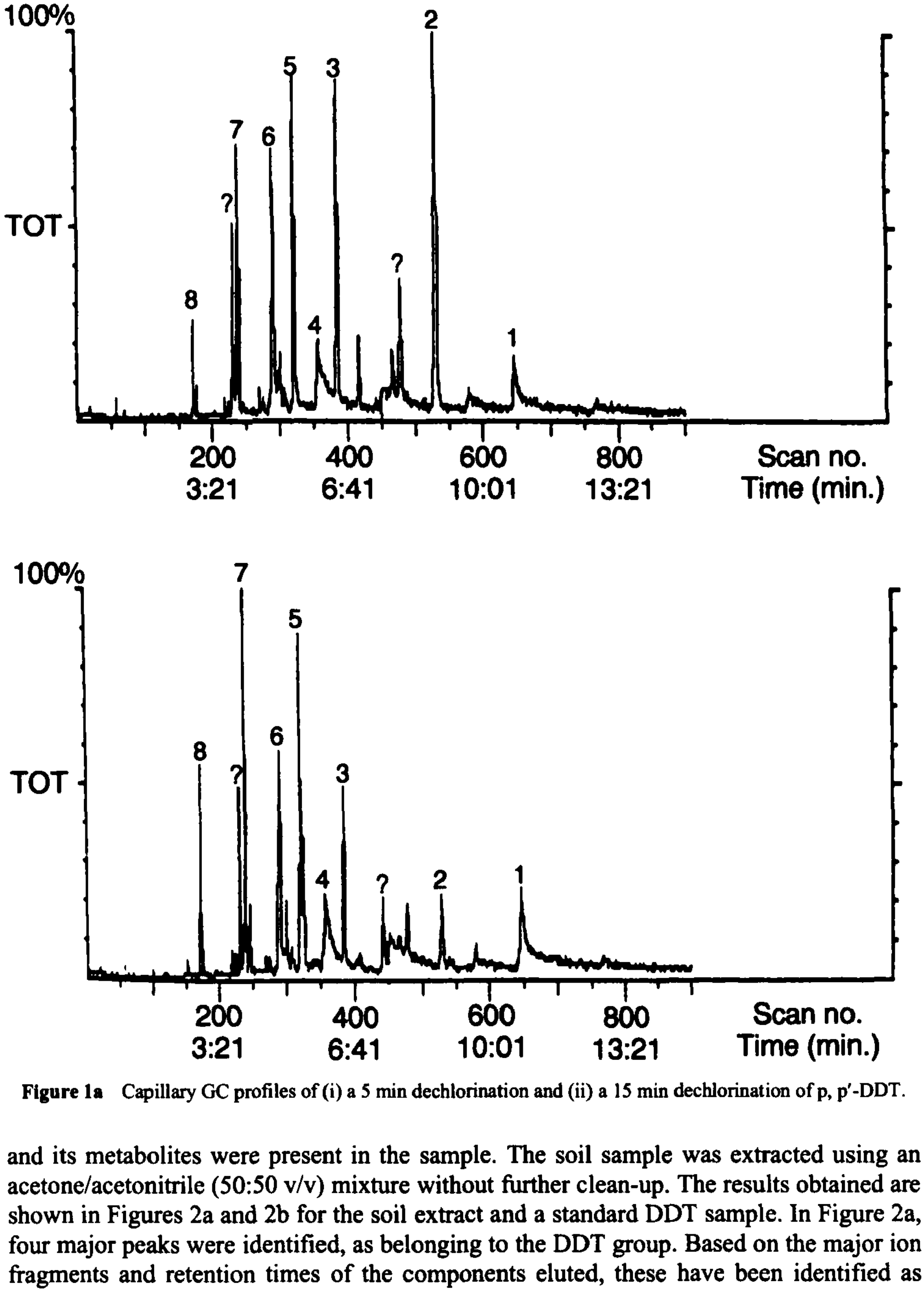

Figure 1a Capillary GC profiles of (i) a 5 min dechlorination and (ii) a 15 min dechlorination of p, p′-DDT.

and its metabolites were present in the sample. The soil sample was extracted using an acetone/acetonitrile (50:50 v/v) mixture without further clean-up. The results obtained are shown in Figures 2a and 2b for the soil extract and a standard DDT sample. In Figure 2a, four major peaks were identified, as belonging to the DDT group. Based on the major ion fragments and retention times of the components eluted, these have been identified as indicated in Table 2. It is evident from Table 2 that all the components identified are metabolites of p, p′-DDT, but pure p, p′-DDT (m/z = 235, $C_{14}H_9Cl_5$) itself was not detected.

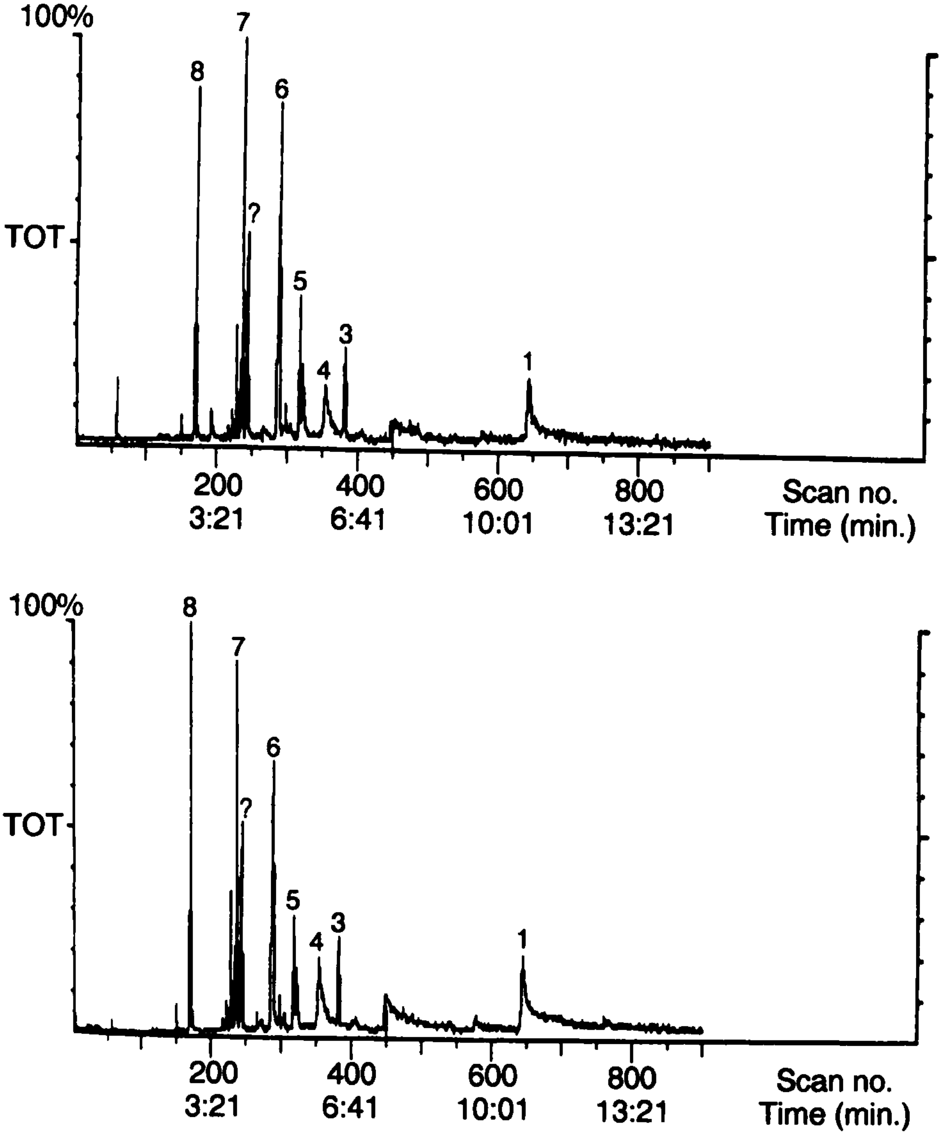

Figure 1b Capillary GC profiles of (i) a 1 h dechlorination and (ii) a 2 h dechlorination of p,p'-DDT.

It is interesting to note that p, p'-DDE (peak 2, m/z = 318) was found in the sample. This was identified on the basis of retention time and the supplementary evidence obtained from its major ion fragments. While peaks 3 and 4, based on retention times could be identified as a DDT derivative, Table 2 quite clearly shows that GC-MS identifies them as metabolites of p, p'-DDT. Both peaks have a molecular formula $C_{14}H_{11}Cl_3$ (see major ions in Table 2). It is apparent from the mass fragments that all have similar spectra consisting of identical components. Finally, peak 1 with m/z = 139 (Figures 2a, 3) was examined and was identified

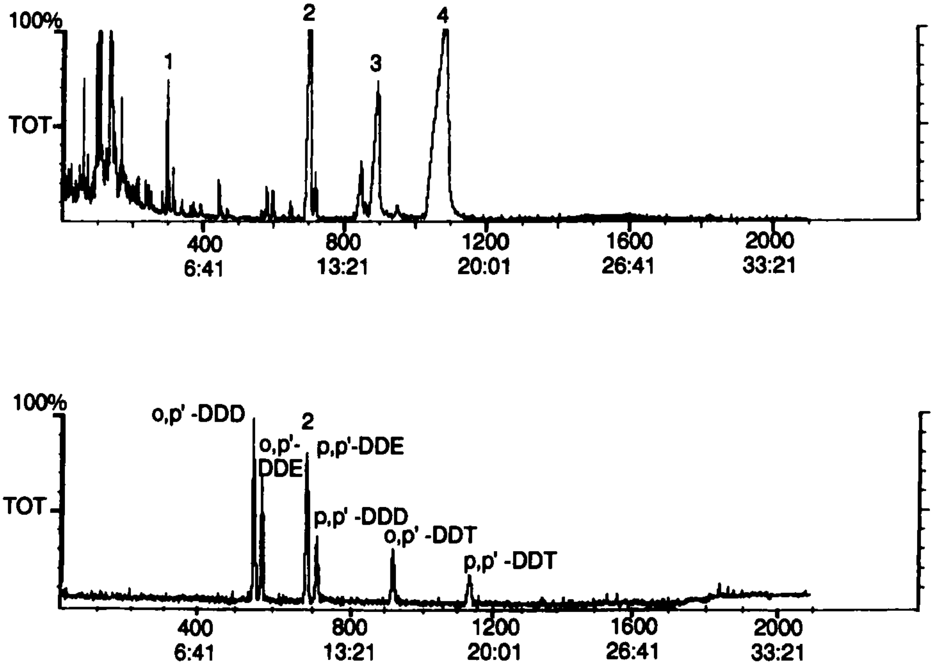

Figure 2 Capillary GC profiles of (a) a soil extract and (b) a standard DDT mixture (o, p'-DDD, o, p'-DDE, p,p'DDE, p, p'-DDD, o, p'-DDT and p, p'-DDT).

as bis-(p-chlorophenyl) methanone from its mass spectrum. The formation of this compound is possible by elimination of the CCl_3 moiety from the C-2 carbon. From this work, it may be reiterated that most of the DDT compounds found in environmental samples undergo degradation to form DDT metabolites. It is also clear that production of degradation intermediates can be useful in the characterisation of components in environmental samples.

Table 2 Major DDT metabolites identified in an environmental sample with their characteristic Ion fragments.

Peak No.	*Compound*	*Major Ions† (m/z)*					
1	$C_{13}H_8OCl_2$	[139],	250,	121,	76		
2	$C_{14}H_8Cl_4$ (p,p'-DDE)	[318],	250,	106			
3	$C_{14}H_{11}Cl_3$*	[284],	212,	235,	51,	250,	
		176,	165,	75,	106,	125,	136
4	$C_{14}H_{11}Cl_3$*	[284],	236,	250,	165,	51,	
		176,	75,	101,	176,	212,	125

† in order of decreasing intensity; [ ] base peak

* identified as that described in Table 1, peak no. 4, compound $C_{14}H_{11}Cl_3$, a metabolite of p,p'-DDT

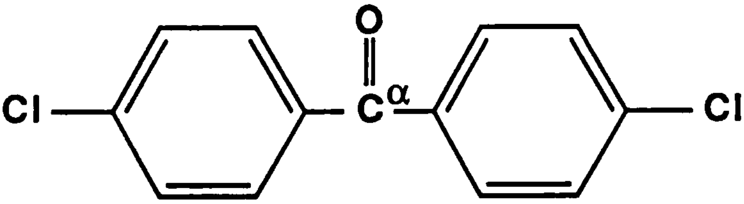

Figure 3 Structure of bis-(p-chlorophenyl) methanone.

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