Dechlorination of p,p′-DDT in Aqueous Media

by J. SINGH and M. MALAIYANDI
Scientific Services Laboratoy,
Canada Department of Agriculture, Ottawa, Ontario

Introduction

It has been reported that the metabolism of p, p'-DDT (1, 1, 1)-trichloro-2, 2-bis(4-chlorophenyl)ethane by avian and mammalian liver has led to the identification and isolation of p, p'-DDD, (1, 1)-dichloro-2, 2-bis(4-chlorophenyl)ethane as one of the major metabolites (1-7). Also, considerable attention has been drawn to the conversion of p, p'-DDT to p, p'-DDD by the microflora of the intestinal tract (8-13). Further, p, p'-DDD was obtained as one of the primary degradation products of p, p'-DDT when the latter was incubated in the medium containing pathogenic and saprophytic bacteria and by several soil micro-organisms such as Aerobacter aerogenes, actinomycetes (14-21). We now wish to report that p, p'-DDT was reduced to give p, p'-DDD as one of the products in aqueous medium under pressure.

Experimental

A. Reaction of p, p'-DDT with granular tin metal in a sealed tube

In a thick-walled borosilicate glass bomb tube (12 x 2. 5 cm.) a sample of 5 mg. of p, p'-DDT was suspended in 15 ml. of distilled water and about 3-5 ml. of p-dioxane was added to get a homogeneous

Bulletin of Environmental Contamination & Toxicology,
Vol. 4. No. 6. 1969. published by Springer-Verlag New York Inc.

solution. After adding 10 g. of granular metallic tin and 0.5 g. of solid ammonium chloride, the bomb tube was sealed and heated at 110-115°C for about 8 hours. The sealed tube was then cooled, cut open at the sealed end and the products were extracted with 5 x 30 ml. portions of petroleum ether (b.p. 30-35°C). Four such experiments were carried out in the same manner and the organic extracts pooled, evaporated under reduced pressure and made to volume (100 ml.). A portion of this solution, after proper dilution, was estimated by gas chromatography to contain p,p'-DDT, p,p'-DDD and p,p'-DDE in the amounts of 0.0, 4-5, and 2-3% respectively.

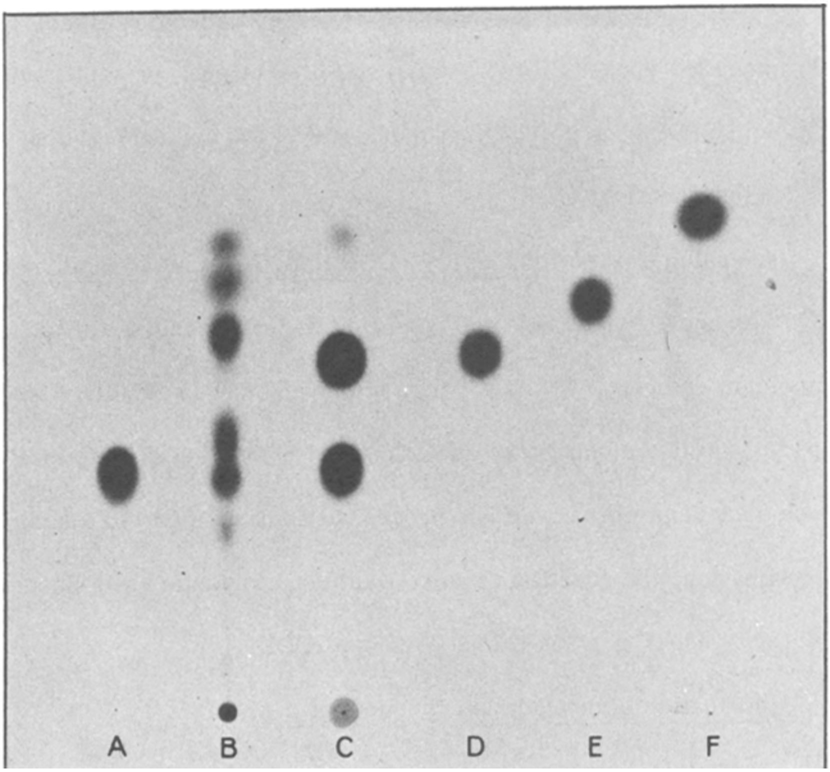
B. Conversion of p,p'-DDT to p,p'-DDD in aqueous medium alone

The above experiment was repeated without granular tin and ammonium chloride. Exactly 5 mg. of p,p'-DDT was dissolved in 3-5 ml. of p-dioxane in the bomb tube and diluted with 15 ml. of distilled water. Three such runs were made and processed as described in Experiment A. On estimation, the reaction mixture was found to contain 40% unconverted p,p'-DDT, 43.5% p,p'-DDD and 4-5% p,p'-DDE.

C. Identification of degradation products of p,p'-DDT

(1) By thin-layer chromatography. - Five silver nitrate-impregnated alumina thin-layer plates were prepared in the usual manner (22) by suspending 30 g. of Alumina G (E. Merck Co.) in 40 ml. of 95% ethanol containing 0.125 g. of silver nitrate. The plates were dried in the dark and preserved over anhydrous silicagel. Reference samples of p,p'-DDD,

p, p'-DDE, o.p'-DDT and p, p'-DDT were spotted along with reaction products of Reactions (A) and (B). The plate was developed in 2% acetone in n-hexane. After developing, the plates were dried and irradiated with a low pressure hydrogen lamp. The chromatogram is shown in Figure 1.



A, D, E, F - Standards of p, p'-DDD, p, p'-DDT, o, p'-DDT and p, p'-DDE.
B - Reaction products from p, p'-DDT with Sn + H_2O.
C - Reaction products from p, p'-DDT with H_2O alone.

(2) By gas-liquid chromatography. - Samples of degradation

products from Reactions (A) and (B) were analyzed in series along with known standards by injecting into a 6' glass column containing HMDS-treated Chromosorb W coated with 6% QF-1 and 4% DC-11 at 200°C. The three major peaks had identical retention times as p, p'-DDT, p, p'-DDD and p, p'-DDE.

Discussion

Farrow *et al.* (23) observed traces of p, p'-DDD in canned spinach produced from permissible residue levels of p, p'-DDT. In order to simulate the conditions employed by these authors, an experiment was designed to treat p, p'-DDT in aqueous medium with granular metallic tin and ammonium chloride in a sealed borosilicate tube. After heating at 110-115°C for a period of eight hours, the reaction mixture was processed and the products were identified by thin-layer chromatoplate technique and gas chromatography.

From the chromatoplate (Figure 1), it can be seen that in this reaction, practically all p, p'-DDT has been degraded to p, p'-DDD, p, p'-DDE and probably p, p'DDA along with three major unknown components. On gas chromatographic analysis, the two major peaks are found to have the same retention times as p, p'-DDE and p, p'-DDD. It is rather surprising that only small amounts of p, p'-DDE and p, p'-DDD (2-5%) are obtained, and other degradation products seem to predominate in this reaction. Also, it is interesting to note that o, p'-DDT could not be detected.

Although it is expected that in Reaction (A) metallic tin would initiate the removal of one of the chlorine atoms to facilitate reduction, it is deemed worthwhile to explore the action of water on p,p'-DDT at the glass surface. With this objective in view, several experiments have been carried out by heating p,p'-DDT in aqueous dioxane in a sealed tube. By thin-layer chromatographic analysis, the three spots have Rf's similar to p,p'-DDT, p,p'-DDD and p,p'-DDE along with probably small amounts of p,p'-DDA. Gas chromatographic analysis indicate that p,p'-DDD (43.5%) is formed more predominantly than p,p'-DDE (3-4%) along with 40% unconverted parent compound.

It would seem that the conversion of p,p'-DDT to p,p'-DDD does happen in aqueous medium under pressure without the assistance of foreign materials. The mechanism of formation of p,p'-DDD and identification of other degradation products are under investigation and will be discussed in detail elsewhere.

Our thanks are due to Dr. J. P. Barrette for his constructive criticism and keen interest in the work.

References

(1) Peterson, J.E. and Robison, W. H. Toxicol. Appl. Pharmacol. 6, 321 (1964)

(2) Klein, A.K., Laug, E.P., Datta, P.R., Watts, J.O. and Chen, J.T. J. Assoc. Offic. Agr. Chemists 47, 1129 (1964)

(3) Bunyan, P.J., Page, J.M.T. and Taylor, A. Nature 210, 533 (1966)

(4) Jeffries, D.J. and Walker, C. H. Nature 212, 533 (1966)

(5) Ottoboni, A., Gee, R., Stanley, R.L. and Goetz, M.E. Bull. Envir. Contam. and Toxicol. 3, 302 (1968)

(6) McCully, K.A., McKinley, W.P. and Phillips, W.E.J. J. Assoc. Offic. Agr. Chemists 51, 1050 (1968)

(7) Ottoboni, A. and Ferguson J.I. Bull. Envir. Contam. and Toxicol. 3, 296 (1968)

(8) Barker, P.S., Morrison, F.O. and Whittaker, R.S. Nature 205, 621 (1965)

(9) Barker, P.S. and Morrison, F.O. Can. J. Zool. 43, 652 (1965)

(10) Miskus, R.P., Blavi, D.P. and Casida, J.E. J. Agr. Food Chem. 13, 481 (1965)

(11) Mendel, J.L. and Walton, M.S. Science 151, 1527 (1966)

(12) McCully, K.A., Villeneuve, D. C., McKinley, W.P., Phillips, W.E.J. and Hideroglu, M. J. Assoc. Offic. Agr. Chemists 49, 966 (1966)

(13) Braunberg, R.C. J. Agr. Food Chem. 16, 451 (1968)

(14) Wedemeyer, G.A. Science 152, 647 (1966)

(15) Chacko, C.I., Lockwood, J.L. and Zabik, M. Science 154, 893 (1966)

(16) Wedemeyer, G.A. Appl. Microbiol. 15, 569 (1967)

(17) Guenzi, W.D. and Beard, W.E. Science 156, 1116 (1967)

(18) Hooper, G.H.S. Proc. Roy. Soc. Queensland 79, 9 (1967)

(19) Johnson, B.T., Goodman, R.N. and Goldberg, H.S. Science 157, 560 (1967)

(20) Mendel, J.W., Klein, A.K., Chen, J.T. and Walton, M.S. J. Assoc. Offic. Agr. Chemists 50, 897 (1967)

(21) Ko, W.H. and Lockwood, J.L. Can. J. Microbiol. 14, 1069 (1968)

(22) Morris, L.J. J. Lipid Research 7, 717 (1966)

(23) Farrow, R.P., Elkins, Jr. E. R. and Cook, R.W. J. Agr. Food Chem. 14, 430 (1966)