Oxidation with Tetrabutylammonium Permanganate for Quantitation of DDT Residues in GLC Determination of Chlorinated Hydrocarbons

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In analysis of environmental pollutants the determination of DDT residues and polychlorinated biphenyls (PCB) is complicated by difficulties in the separation of the two groups of compounds. Especially the interference of DDE (2,2-bis-(p-chlorophenyl)-1,1-dichloroethylene) with certain constituents of PCB is a serious problem (BEVENUE et al. 1969), and methods have been developed, utilizing chromic acid in acetic acid for oxidation of DDE to DBP (p,p´-dichlorobenzophenone). This reagent has been used in a method for quantitation of pesticides by TLC (BUSH et al. 1973) and also in the determination by GLC of DDT residues as DBP (MILES 1972). In the last case the oxidation of DDT (2,2-bis-(p-chlorophenyl)-1,1-dichloroethane) is accomplished after previous dehydrochlorination with 1,5-diazabicyclo 5.4.0 undec-5-ene to DDE and DDMU (2,2-bis-(p-chlorophenyl)-1-chloroethylene) respectively.

The present paper describes a method for conversion in a single step of DDT, DDE, DDD and DDMU to DBP for subsequent GLC quantitation of the total content of neutral DDT metabolites.

The proposed method takes advantage of the facile ion pair extraction of permanganate ion from water to low polar solvents observed on the addition of lipophilic ions like tetrabutylammonium ion. This technique has been used by STARKS (1971) to perform a rapid two-phase oxidation of 1-undecene in benzene.

In the present case, anisol is used as a high boiling solvent of the desired properties, especially low response to the electron capture detector and sufficient stability under the conditions used.

The two-phase reagent, in addition to tetrabutylammonium permanganate, contains sodium periodate and sodium hydroxide. The reagent thus fulfills three separate functions viz (a) rapid dehydrochlorination of DDT and DDD, (b) regeneration of permanganate during the oxidation and (c) rapid oxidation to DBP of a proposed intermediate, 4,4´-dichlorobenzilic acid (cf below).

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METHOD

Standards:

DBP (Mp 146°, prepared as described by HALLER et al. (1945);
(165 mg/l in hexane).
DDE (Analytical Standards; 202 mg/l in hexane).
DDD (" " 201 " ")
DDT (" " 252 " ")
o,p-DDT (" " 216 " ")

Solvents:

n-Hexane (KEBO; Kp 66-69° C, distilled).
Anisol (Merck, Zur Synthese, distilled; Bp 154-155°C).
Water (Distilled, extracted with hexane to remove disturbing impurities (LEVI et al. 1972).

Apparatus:

Centrifugation tube (15 ml) with teflon screw cap.
Teflon coated magnet 5 x 10 mm.
Combined magnetic stirrer and heater.

Reagents:

Tetrabutylammonium hydroxide solution; Tetrabutylammonium hydrogen sulfate (Fluka; 6,8 g, 20 mmol) was dissolved in sodium hydroxide solution (2M) to 100 ml.

Permanganate-periodate solution. Sodium periodate (Merck, Zur Analyse; 10,7 g, 50 mmol) and potassium permanganate (Merck, Zur Analyse; 3,85 g, 25 mmol) were dissolved in water to 100 ml.

Sulfite solution. Sodium sulfite (Merck, Zur Analyse);
1 M solution in water.

OXIDATION PROCEDURE

From a thin layer chromatogram (0.25 mm Silicagel HF) of the compounds studied, containing DDT residues in amounts corresponding to 0,2 - 20 µg DDE, a 15 cm^2 zone was scraped off and transferred to a centrifugation tube. Anisol (200 µl) was added. (Alternatively, a purified extract in hexane was added to 100 mg silicagel and carefully concentrated to dryness whereafter 200 µl anisol was added.)

To the tube was added equal volumes (1 ml) of the tetrabutylammonium hydroxide and the permanganate-periodate solutions. The tube was heated under magnetic stirring in a bath (100 °C) for 30 min. The mixture was cooled and hexane (0,5 ml; internal standard hexachlorobenzene; 0,1 µg/ml) and the sulfite solution (2 ml) was added. The mixture was shaken for 30 seconds and the layers were allowed to separate (3-5 min.).

For quantitation the organic layer was injected (1-3 µl), directly or after appropriate dilution into a Varian 1400 gas chromatograph fitted with an electron capture detector. The 160 cm all-glass column (i.d. 0,18 cm) was filled with 4% SF 96 methyl silicone oil on 100-120 mesh silanized Chromosorb W. The oven temperature of 195° C gave DBP a retention time of ca 3.5 min.

OXIDATION OF DDT ON A PREPARATIVE SCALE

To a solution of DDT (3,54 g; 10 mmol) in anisol (50 ml) was added potassium permanganate (7,9 g; 50 mmol) and tetrabutylammonium hydrogen sulfate (17 g; 50 mmol). The mixture was stirred at 20°C for 72 hrs with aqueous sodium hydroxide (2M, 200 ml) and was then acidified with sulfuric acid, whereupon sodium sulfite was added.

The acids present together with DBP and traces of DDE in the organic phase were isolated via sodium hydrogen carbonate extraction and characterised by TLC (Silicagel HF; methanol - isopropyl ether 1:4). Rapid crystallisation of the crude acid product (1.0 g) yielded 4-chlorobenzoic acid (240 mg), recrystallised from ether-hexane (mp 240-242°) and identified by comparison with an authentic sample (mixed m.p., TLC, IR).

From the mother liquor 4,4'-dichlorobenzilic acid was isolated as a copper complex (m.p. 206-207°; 540 mg) on the addition of a solution of copper acetate (1 g) in methanol-water (1:1; 100 ml). The free acid was obtained crystalline on treatment of the complex with a 1:1 mixture of hexane and sulfuric acid (1M) for 24 hrs (magnetic stirring). M.p. 111-114° (Found C 56.5; H 3.8; Cl 24.3. $C_{14}H_{10}Cl_2O_3$ (297.1) requires 56.6; H 3.4; Cl 23.9). MONTANGE (1902) gives m.p. 101°, 75.

The acid was further characterized by its mass spectrum, which showed pertinent peaks at m/e = 296 (M^+; 0.5% of base peak) 251, 139 (base peak), 111 and 75 with fragmentation and isotopic patterns consistent with the behavior of bis-(p-chlorophenyl)-methanol derivatives (SPHON et al. 1970).

RESULTS AND DISCUSSION

The recoveries of DBP from DDT, DDE and DDD at levels corresponding to 0.2, 2.0 and 20 µg DDE respectively were quantitative (101 ± 3%), with somewhat high recovery values at the 0,2 µg level, probably dependent on interfering impurities in reagents and equipments (LEVI et al. 1972).

Prolonged reaction time (2 hrs), including a second addition of the permanganate-periodate solution (1 ml) after 1 hour, did not change the recoveries of DBP from DDE in the tested interval, but a reaction time of 15 min. resulted in significantly lower recoveries at the 2.0 and 0.2 µg levels.

The less reactive o,p´-DDT (2-o-chlorophenyl-2-p-chlorophenyl-1,1,1-trichloroethane) required a modified addition of reagents (3 ml each of tetrabutylammonium hydroxide and permanganate-periodate solutions) for quantitative recovery of o,p´-DBP (o,p´-dichlorobensophenone) at 0.5 h reaction time, as evident by comparison with recoveries by the chromic acid technique (MILES 1972) from o,p´-DDE (2-o-chlorophenyl-2-p-chlorophenyl-1,1-dichloroethylene) in a few experiments at the 20 µg level.

The described oxidation of DDT, DDD and o,p´-DDT are preceded by a dehydrochlorination reaction, complete within a few min. under the strongly alkaline conditions used. Hence the described results cover also DDMU and o,p´-DDE.

The oxidations of the ethylenic bonds are probably initiated by the formations of cyclic manganese esters as generally postulated for this type of reactions (STEWART 1965). These might decompose with direct formation of dichlorobensophenone or via 2,2´-dichlorodiphenyl- glycol derivatives and the corresponding α-hydroxy-carbonyl compounds. The latter path might explain that the recovered amounts of DBP at short reaction times do not account for the DDE consumed at the 0.2 and 2.0 µg levels. Further evidence for significance of that path is given by the isolation of 4,4´-dichlorobenzilic acid from the reaction mixture after oxidation of DDE on a preparative scale in the absence of periodate.

The 4-chlorobenzoic acid, isolated in the same experiment, is supposed to originate from an oxidation via 4-chlorophenylglyoxylic acid of 4,4´-dichlorobenzilic acid at prolonged contact with manganese oxides (STEWART 1965) in a reaction somewhat similar to the oxidation by permanganate of triphenyl carbinols to bensophenones (BANOO et al. 1969). In support of this view, TLC analysis of the reaction mixture indicated the presence of a ketoacid. This side reaction is, however, suppressed in the presence of periodate wich selectively oxidizes α-hydroxyacids to the corresponding aldehydes or ketones (YANOKA et al. 1968), and as mentioned above also serves to regenerate the permanganate during the reaction (LEMIEUX et al. 1955).

The choise of anisol as an organic solvent for the two-phase reaction is primarily motivated by its physical properties. However, anisol is a moderately activated aromatic compund and probably also serves to minimize nuclear oxidation of DBP and related deactivated compounds. The composition of a low chlorinated PCB mixture (Chlophen A 30), e.g., was not detectably changed on treatment with the reagent under standard conditions.

The proposed two-phase oxidation method combines the use of small volumes of organic solvent with the rapid performance of the entire process in a single vessel. Especially the need of washing of the final extract after reduction of excess permanganate is eliminated by the addition of an adjusted volume of hexane which enhances the partition towards the water phase of disturbing ion pairs.

The combination of the oxidation method with suitable clean up procedures should give valuable aids in the determination of DDT and its low polar metabolites by allowing a simple quantitation of their sum as DBP. Alternatively the procedure will serve to simplify the determination of PCB compounds by elimination of interfering peaks. Similar ion pair techniques would have wide applicability e.g. in other fields of pesticide analysis.

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