blanks are obtained with the natural material in the latter procedure. This is most probably due to the fact that the carbohydrate present in the extracts is not retained on the column and yields interfering carbonyl compounds on acid hydrolysis. Four-tenths per cent of OXDAPRO added to *Cicer arietinum* or *Cajanus cajan* flour can be recovered (85–90% yield). In about 570 different samples of *Lathyrus sativus* analyzed by Nagarajan and Gopalan (1968), the range of OXDAPRO content varied from 0.1 to 2.5%, about 10% of the samples having 1–1.2%, 3% of the samples having 2–2.5%, 38% in the range 0.5–1%, and 16% in the range 1.2–1.6%. The presence of up to 50% *Lathyrus sativus* in the flours of *Cicer arietinum* or *Cajanus cajan* did not cause any analytical problems in the present procedure. With very low neurotoxin content, larger samples (10 g) have to be taken so that even traces can be detected by the present procedure. It is probable that the method can be further scaled down and sensitivity increased by fluorimetric methods in the coupled lactic dehydrogenase assay. The present method is recommended only when absolute confirmation for the presence of bound DAPRO is needed.

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Anaerobic Degradation of 1,1,1,2-Tetrachloro-2,2-bis(*p*-chlorophenyl)ethane (DTE)

DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene) is the major product from the anaerobic degradation of 1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane (DTE). This is the same reaction that is observed with electrochemical reduction. It is postulated that electrochemistry may be used as a means of predicting the products formed from the anaerobic reduction of organochlorine compounds.

DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane) has been shown to be the major degradative product of DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) under anaerobic conditions (Guenzi and Beard, 1967). DDD is also the first product formed in the electrochemical reduction of DDT (Farwell, 1973; Rosenthal and Lacoste, 1959). We questioned whether or not other compounds might give the same products from anaerobic degradation as they do from electrochemical reduction and if, therefore, electrochemistry could provide insight into the environmental degradation of pesticides under anaerobic conditions. As a first step in this investigation we studied the degradation of a DDT analog, 1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane (DTE), under flooded soil conditions and compared the degradation products with the electrochemical reduction products of DTE.

EXPERIMENTAL SECTION

Air-dried Bowdoin soil (pH 7.9, 1.44% organic carbon, 0.8% sand, 30.6% silt, 68.6% clay) was passed through a 35 mesh sieve and treated with DTE (Aldrich, puriss grade) in acetone to give a total DTE concentration of 100 ppm. After air drying for 1 hr the soil was amended with ground alfalfa (5% w/w) and fresh soil (5% w/w), the latter to ensure the presence of microbes. After mixing the soil for 1 hr, 100-g portions were transferred to amber bottles, flooded with water to a depth of 1 in., plugged with a gauze stopper, and incubated at room temperature.

At 2-week intervals the soil samples were transferred to a soxhlet apparatus and extracted for 3 hr with redistilled acetone. The acetone was evaporated *in vacuo* and the residue partitioned into redistilled hexane. The hexane was concentrated and the extract passed through a Florisil column (100–120 mesh, Floridian Co.) while eluting with hexane.

We were unable to separate DTE from DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene) (Aldrich, 99%) by gas chromatographic procedures and therefore we used high-pressure liquid chromatography. A Waters Associates ALC 202 liquid chromatograph equipped with a U.V. detector (254 nm) was used. The detector response for DTE was less than a tenth of that for DDE. The operating conditions were as follows. The column was C_{18}/Corasil packed in a 2 ft × $^1/_8$ in. stainless steel column; the elution solvent was methanol–H_2O (67:33); flow of 1.2 ml/min.

All compounds were incubated in triplicate samples of soil.

RESULTS AND DISCUSSION

The first product in the sequential, electrochemical reduction of DTE is the formation of DDE (Farwell, 1973;

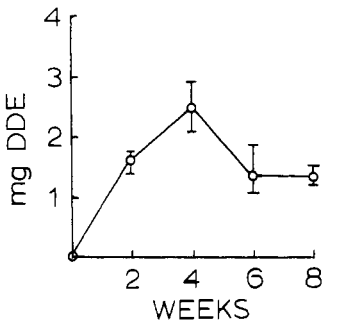
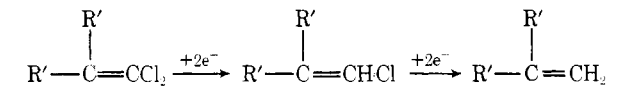


Figure 1. Anaerobic formation of DDE from DTE: (O) mean of three replicate samples (vertical bars represent range of samples).

Rosenthal and Lacoste, 1959). This is a classic electrochemical reaction; when adjacent chlorines are present on a saturated system two chlorines are lost in a one-step reduction with the simultaneous formation of a double bond (Mann and Barnes, 1970). The same process appears to occur under flooded soil conditions. As Figure 1 demonstrates, there is a steady increase in DDE concentration until week 4 when there is a decrease. The corresponding decrease in DTE is not presented in Figure 1, since it could not be detected after day 1 due to the weak detector response. The period up to week 4 appears to follow first-order kinetics as has been previously observed for the degradation of pesticides under anaerobic conditions (Hill and McCarty, 1967). To confirm the formation of DDE a sample from week 8 was evaporated and its ir spectrum obtained. This was identical with the spectrum of DDE. Under the same incubation procedure DDT was completely converted into DDD in 4 weeks.

After week 4 there is a decrease in the DDE concentration. This could be due to the formation of further reduction products. For instance, the electrochemical reduction products of DDE are (Farwell, 1973; Rosenthal and Lacoste, 1959)



where R′ = (C_6H_4Cl)–.

We did not, however, detect any of these compounds in our anaerobic system, which supports Plimmer's *et al.* (1968) claim that DDE is not reduced. The electrochemical reduction of DTE to DDE in dimethyl sulfoxide–tetraethylammonium bromide occurs at less than −1.240 V (*vs.* sce) while DDE reduces at −1.757 V (Farwell, 1973). This latter value is 0.517 V more cathodic than the reduction potential of −1.240 V found for DDT. These data imply that while the factors (biological and/or chemical) which promote the anaerobic degradation of organochlorine compounds can generate a sufficient redox potential (*Eh*) to reduce DDT and DTE, this potential is not low enough to degrade DDE. Instead, the observed decrease of DDE could be due to its irreversible binding to the soil.

Thus it appears that reductive electrochemistry might possibly be used to predict if organochlorine compounds will degrade under anaerobic conditions and what products will be formed. This can be further demonstrated with lindane which under flooded soil conditions loses adjacent chlorines with concomitant formation of a double bond to give γ-3,4,5,6-tetrachloro-1-cyclohexene (Tsukano and Kobashi, 1972), a process which also occurs electrochemically at −1.521 V.

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