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Environmental Contamination and Toxicology

Dechlorination of DDT by Electrocatalytic Hydrogenolysis

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The insecticide DDT (1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane) is credited with saving millions of lives during and after WWII in fighting insect-borne diseases and is still used for disease control in parts of Africa, Asia and Latin America (Turusov et al., 2002). Low application rates, low acute mammalian toxicity and low manufacturing costs led to widespread residential and agricultural use of DDT, to the extent of >400,000 t yr^{-1} worldwide by the 1960s. DDT's environmental persistence initially seemed advantageous because it decreased the frequency of application, although even by 1946 exposure to DDT was known to be lethal to non-target organisms such as fish and birds. DDT's toxicity to reptiles and amphibians, and its association with calamitous declines in the reproductive success of birds of prey, led to a ban on DDT in western countries by the early 1970s (Bunce, 1994). DDT's lipophilicity causes it to concentrate in fatty tissue, especially in species high in the food chain; recent reports include unacceptably high levels of DDT in human breast milk in Mexico and Thailand (Turusov et al., 2002). DDT's low but finite volatility allow it to travel via the atmosphere and hence to impact biota far from its point of use. DDT and its degradation product DDE are weak xenoestrogens, and some evidence of carcinogenicity has been reported (Vieira et al., 2001). DDT sorbs strongly to soil organic matter with half lives of several years in temperate climates (Vieira et al., 2001). No completely practical method for remediating DDT-contaminated soils yet exists. Bioremediation is inefficient due to DDT's low water solubility and its chlorine substitution which inhibits metabolism; its metabolic products are also persistent environmentally (Smith et al., 2004). UV photolysis is inefficient (Chu, 1999); thermal destruction is costly and can afford chlorinated dibenzodioxins and dibenzofurans as by-products. Adsorption onto granular activated carbon merely transfers the contaminant from the soil matrix onto GAC.

Several authors have dechlorinated DDT electrolytically, but efficient and complete aliphatic and aromatic dechlorination remains elusive. DDE and DDD were major products at Pt, Pd, Rh, and Ni cathodes; DDE, DDNU and 1,1-DPE were formed in ethanol, acetonitrile and dimethylformamide (Udovick, 1979). Figure 1 gives the names and structures corresponding to these abbreviations.

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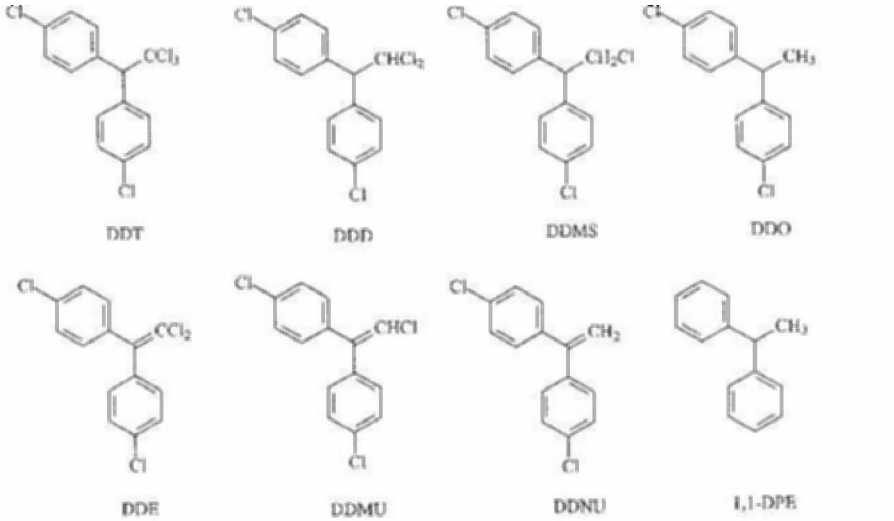

Figure 1. Names and chemical structures of DDT and its derivatives. Names, in order, are 1,1-(bis-4-chlorophenyl)-2,2,2-trichloroethane (DDT); 1,1-(bis-4-chlorophenyl)-2,2-dichloroethane (DDD); 1,1-(bis-4-chlorophenyl)-2-chloroethane (DDMS); 1,1-(bis-4-chlorophenyl)-2,2-dichloroethene (DDE); 1,1-(bis-4-chlorophenyl)-2-chloroethene (DDMU); 1,1-(bis-4-chlorophenyl)-ethene (DDNU); 1,1-(bis-4-chlorophenyl)-ethane (DDO); 1,1-diphenylethane (1,1-DPE).

Cyclic voltammetry in acetonitrile indicated four sequential reduction steps (Udovick, 1979). Amperostatic reduction in methanol, at an Hg pool cathode, gave primarily DDE, with small amounts of DDD, DDMU, DDMS, DDNU and DDO; potentiostatically, DDO and DDMS were major products (Merica et al., 1999). DDO was formed at a Pb cathode in an aqueous emulsion of heptane and Triton SP-175 with mass balances > 97% but low current efficiency (Merica et al., 1999). Electrolyses of DDT mediated by *tris*-(2,2'-bipyridyl)cobalt(II) salts led to aliphatic dechlorination, while both aliphatic and aromatic dechlorination were achieved in a bicontinuous microemulsion of water, dodecane, and didodecyldimethylammonium bromide (Schweizer et al., 1994).

Here, we report aliphatic and aromatic dechlorination of DDT by electrocatalytic hydrogenolysis (ECH), which involves electrolysis of a protic solvent at a noble metal cathode, usually Pd, to give hydrogen atoms. These react with an adsorbed organic substrate on the metal surface (M), eq. [1]-[4] (Dabo et al., 1999, 2000).

[1] H_2O (or H_3O^+) + e^- + M → $H_{ads}M$ + OH^- (or H_2O)

[2] R-Cl + M → $(R\text{-}Cl)_{ads}M$

[3] $(R\text{-}Cl)_{ads}M$ + $2H_{ads}M$ → $(R\text{-}H)_{ads}M$ + HCl

[4] $(R\text{-}H)_{ads}M$ → R-H + M

The efficiency of ECH depends on current density, electrode potential, and the nature and material of the electrode surface. Hydrogen evolution (eq. [5]-[6]) competes with ECH, lowering the current efficiency.

[5] $H_{ads}M + H_2O + e^- \rightarrow H_2 + M + OH^-$

[6] $H_{ads}M + H_{ads}M \rightarrow H_2 + 2M$

Dabo et al. (1999) developed a cathode for ECH by embedding catalyst particles (5% Pd on Al_2O_3) in a reticulated vitreous carbon matrix. This system, which has been described in detail by Dabo et al. (1999) and by Stock and Bunce (2002), achieved nearly complete dechlorination of pentachlorophenol (Dabo et al., 2000), and complete and rapid dechlorination of atrazine (Stock and Bunce, 2002).

MATERIALS AND METHODS

HPLC grade solvents, anhydrous sodium sulphate, and sulphuric acid were obtained from Fisher Scientific (Toronto, ON); 5% Pd/Al_2O_3, DDT, DDE, and DDD from Aldrich (Mississauga, ON); tetrabutylammonium perchlorate from Kodak (Rochester, NY); DDMU, 100µg/mL, from Accustandard (New Haven, CT); 1,1-DPE, ~92%, from Nisseki Chemical (Pasadena, TX). DDMS and DDNU were available from a previous project (Merica et al., 1999). MilliQ water had resistivity > 10 MΩ cm. RVC and Ti/IrO_2 electrodes were purchased from Electrosynthesis Co. Inc. (Lancaster, NY). Nafion membrane N417 was obtained from Ion Power (New Castle, DE).

For electrocatalytic hydrogenolysis the electrochemical cell was powered by a Princeton Applied Research Model 363 Potentiostat/Galvanostat. The anolyte was 1 M sulphuric acid; in initial trials the catholyte was 25 ppm DDT in 1:1 methanol: 0.01M Na_2SO_4, subsequently adjusted to 25 ppm DDT in 1:1 acetonitrile: water with 0.07 M tetrabutylammonium perchlorate. Further experiments carried out in duplicate with four variables, each at three levels (see Table 1).

Table 1. Experimental conditions for electrocatalytic dechlorination of DDT.

Current (mA)	Catalyst Amount (mg)	Concentration of DDT (ppm)	Concentration of Water (%)
150	50	25	5
150	50	25	15
150	50	25	50
150	20	25	50
150	150	25	50
100	50	25	50
220	50	25	50
150	50	10	50
150	50	15	50

The cathode was an 80 ppi RVC disc (5 mm thick, 36 mm diameter), with a glass-enclosed copper wire lead. The anode was 42 mm x 12 mm x 0.1 mm Ti/IrO_2 with a copper lead. The catalyst powder (5% w/w Pd/Al_2O_3) in the cathode

compartment was stirred into the RVC matrix with a cross-shaped magnetic stir bar. A 100 mL volume of catholyte was needed to allow enough circulation of the catholyte to impregnate the catalyst into the RVC matrix.

HPLC analyses employed either a Waters system equipped with Rheodyne injector, Waters Model 600E system controller, model 486 tuneable absorbance detector, and Millennium^{32} data acquisition package, or an Agilent Model 1100 instrument equipped with Model G1322A quaternary pump and vacuum degasser, Model G1313A autosampler, Model G1315 diode array detector, Model G1316 thermostatted column controller, and Chemstation Version 9 data acquisition package. We used a 3.9 x 300 mm Waters µBondapack C_{18} reverse-phase column, operated with 55% acetonitrile/45% water at 2.5 mL min^{-1}, initial injection volume 20 µL, and (for the Waters HPLC system) detection at 230 nm for all analytes. HPLC solvents were either filtered through 0.45µm Nylon 66 membranes or used in conjunction with a vacuum degasser. Aliquots (0.8 mL) were removed by disposable 1 mL syringe for analysis at 0, 2, 4, 6, 10, 15, 20, 25 and 30 min except for the trials at 100 mA when samples were collected at 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45 min. After allowing any catalyst inadvertently removed to settle, samples were transferred to autosampler vials. Analytes were identified by comparing HPLC retention times with those of authentic samples, and quantified by external standardization ($R^2 > 0.99$ for all sample sets).

RESULTS AND DISCUSSION

Of several C_{18} HPLC columns studied during method development, only Waters µBondapack C_{18} gave adequate resolution of all analytes. Methanol-water mobile phases caused DDT to precipitate from solution upon injection into the HPLC; even with acetonitrile-water, it was expedient to include a 15-minute wash of 100% acetonitrile after every three injections to avoid carry-over. Retention times (min) for the various analytes under the stated analytical conditions were DDT, 30.5; DDD, 19.4; DDMS, 17.0; DDO, 20.8; DDE, 34.9; DDMU, 27.6; DDNU, 25.7; 1,1-DPE, 9.3. The appearance and disappearance of these analytes with time indicated the main reaction sequence as DDT → DDD → DDMS → DDO → 1,1-DPE, with DDT → DDE → DDMU → DDNU → 1,1-DPE as a minor route. DDE was rarely detected on account of rapid further reaction. Quantitative reproducibility of the reaction rates was hampered by sorption of $H_2(g)$ onto the Nafion membrane that separated the anolyte and catholyte, causing an overload on the galvanostat. The bubbles were removed periodically by shaking the whole apparatus.

The rate of disappearance of DDT increased with increasing concentration. Because ECH involves electrochemical reduction of a protic solvent to hydrogen atoms, we hoped to use aqueous methanol as the solvent, but solubility considerations required the use of aqueous acetonitrile. Figure 2 shows a typical time course for the reaction. Mass balances were > 80% at low conversion, but

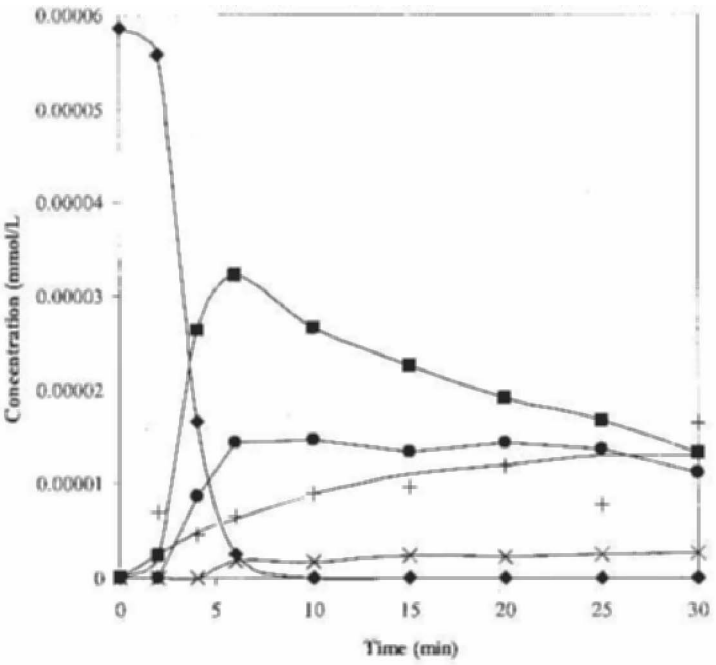

Figure 2. Typical time-course of ECH reaction of DDT: DDT, 25 ppm; water content in catholyte, 50%; applied current 150 mA; catalyst 50 mg; symbols: ♦ = DDT; ■ = DDD; × = DDMS; ● = DDO; • = DDMU; + = 1,1-DPE

fell to < 20% at complete conversion, due to the presence of products lacking an aromatic chromophore.

Both the rate and extent of reduction of DDT increased with the concentration of water in the catholyte; at 5% water, only traces of DDE, DDD and 1,1'-diphenylethane were formed. The lag time previously observed for ECH using a Pd catalyst increased at low water concentration, consistent with the explanation that hydrogenolysis requires the Pd particles to be saturated with hydrogen (Stock and Bunce, 2002). Mass balances were highest at low applied current and low initial DDT concentration, but current efficiencies were consistently < 0.015%, indicating that most hydrogen atoms formed by electrolysis were not used productively.

The amount of catalyst (5% w/w Pd/Al_2O_3) did not greatly change the time required for complete disappearance of DDT, but higher catalyst loadings caused more extensive dechlorination, allowing multiple dechlorination steps to occur before the molecule left the RVC-catalyst matrix. At low catalyst loading, DDD was the major product, representing the loss of one chlorine atom (Figure 3).

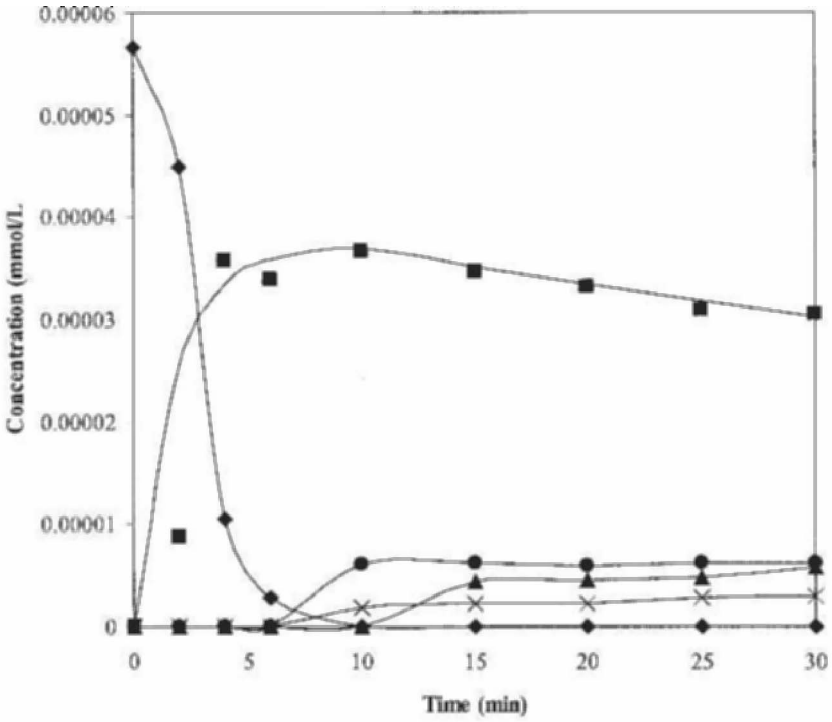

Figure 3. Time course for ECH reaction of DDT at low catalyst loading: DDT, 25 ppm; water content in catholyte, 50%; applied current 150 mA; catalyst 20 mg; symbols as Figure 2.

At high loading of the catalyst, complete dechlorination to 1,1-DPE (50%) was observed (Figure 4). The rate of disappearance of DDT and the extent of dechlorination increased with applied current, although at the expense of both joule heating of the solution, and a greater problem of bubbles of $H_2(g)$ adhering to the membrane.

In conclusion, electrocatalytic hydrogenolysis afforded complete aromatic dechlorination as well as aliphatic dechlorination of DDT, a result not achieved by direct electrolysis. The positive feature of the work is that even aromatic $C(sp^2)$—Cl bonds were cleaved under ECH conditions at ambient temperature and pressure; against this, the high strength of these bonds caused the current efficiency to be very low. Further work at elevated temperatures may establish whether a practical ECH technology for degradation of DDT is achievable. Matsunaga and Yasuhara (2005) have recently shown that DDT can also be completely dechlorinated using sodium naphthalenide as an electrochemical

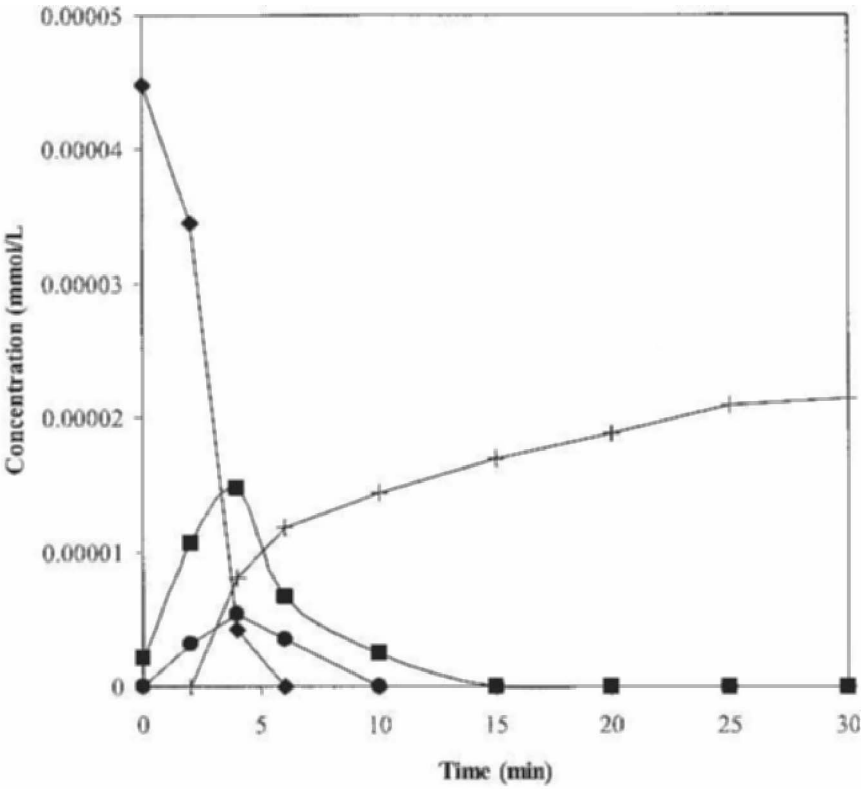

Figure 4. Time course for ECH reaction of DDT at high catalyst loading: DDT, 25 ppm; water content in catholyte, 50%; applied current 150 mA; catalyst 150 mg; symbols as Figure 2.

mediator – the disadvantage of this technique is the need for a completely anhydrous solvent such as DMF.

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