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Electrolytic Dechlorination of DDT In a Bicontinuous Microemulsion

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ABSTRACT

Electrolytic reduction in a bicontinuous microemulsion of surfactant, oil, and water removed aliphatic and aromatic chlorines from DDT. Microemulsions of didodecyldimethylammonium bromide/dodecane/water used with graphite felt cathodes provided a less expensive, less toxic approach to DDT electrolysis compared to using conventional organic solvents and metal electrodes. Good rates of aliphatic dechlorination were achieved by applying -1 V vs. Ag/AgBr and using the catalyst Co(bpy)₃²⁺, but the best yield (34% in 3 hr) of the fully dechlorinated hydrocarbon 1,1-diphenylethane was achieved by using -2 V with oxygen in the reaction medium.

INTRODUCTION

Organohalides such as DDT (1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane) have been used as insecticides since the 1940s and persist worldwide in soils, sediments and ground waters. DDT is resistant to degradation by light and oxidation in the environment. Bacterial decomposition and chemical hydrodechlorination are pathways for natural degradation, which occurs very slowly (1).

Many microorganisms transform DDT to DDD (1,1-bis-(4-chlorophenyl)-2,2-dichloroethane) under anaerobic conditions (1). For example, *A. aerogenes* and *E. coli* convert DDT to DDD and other metabolites (2). Soil microbes (*Actinomycetes*) (3) and yeast (4) also degrade DDT. Reduced coenzymes, porphyrins, and metalloproteins can reductively dechlorinate DDT (5).

Studies mentioned above show that replacement of aliphatic chlorine by hydrogen occurs in the slow environmental degradation of DDT. Because of the persistence of DDT in the environment and its bioaccumulation in the food chain, the search for efficient methods for its degradation is pressing. Previously developed methods have been based on chemical, photochemical, microbiological or electrolytic transformations (6-16).

Effective catalytic reductions employing transition metals (Pt, Pd, Rh, Ni) have been studied (6). Up to 62% chlorine is rapidly lost from DDT by the catalytic action of NiB₂ with NaBH₄ as reductant (7). In a pulse microreactor at 220°C and 2.3 bar H₂ with Pd on α -Al₂O₃ as catalyst, DDE (1,1-bis-(4-chlorophenyl)-2,2-dichloroethene) was obtained (8). 100% conversion to DDE was achieved using Pd on activated carbon in an autoclave under H₂ pressure at 23°C in ethanol/NaOH (9). Reaction of Vitamin B_{12s} with DDT yields DDD and DDE (10). In a system containing the semiconductor TiO₂ with simulated sunlight, DDT had a half life of 46 min and was transformed to HCl and CO₂ (11).

DDT has been destroyed by direct photolysis with UV-light or γ -radiation. Upon anaerobic irradiation in 2-propanol with 253.7 nm light, DDT is dechlorinated to DDD (12). Only reaction products of aliphatic dechlorination are obtained, which are still relatively toxic. Similar results were obtained upon irradiation with ⁶⁰Co (13).

General conclusions from the above studies of DDT reduction are that aliphatic chlorines are easier to remove than aromatic chlorines. There are few reports of the complete dechlorination of DDT to hydrocarbon products. Investigations on the biodegradability and metabolism of DDT are consistent with these conclusions. For example, the enzyme cytochrome P450 with NADPH induces reductive dechlorination of DDT to DDD under anaerobic conditions (14), but dechlorination at aromatic sites is not achieved.

Reduction of aliphatic Cls of DDT has been studied in aqueous/organic solvent mixtures by polarography in buffers of varying pH (15). Electrogenerated O_2^- in DMF rapidly dehydrochlorinates DDT to DDE which can be further oxygenated to 4,4'-dichlorobenzophenone (16). To our knowledge, electrolytic methods feasible for full dechlorination have not been examined. DDT is a particularly relevant test compound, since it has multiple chlorines attached to both aliphatic and aromatic sites and produces many products which can be further dechlorinated.

Although pesticides like DDT are almost totally insoluble in water, they are dispersed widely in the environment in sediments and soils which contain water. Therefore, it is advantageous to design dechlorination processes that can be used in the presence of water. We showed previously that surfactant based fluids containing water can be used for electrochemical catalytic dehalogenations of polychlorinated biphenyls (PCBs) and aliphatic organohalides (17-19).

More recently, we found that bicontinuous microemulsions are particularly advantageous for dechlorination of nonpolar organohalides because of better solubilization and mass transport properties compared to micelles, dispersions, and oil-in-water microemulsions (18,19). Microemulsions are clear, thermodynamically stable, microheterogeneous mixtures of oil, water, and surfactant, and sometimes require a cosurfactant. We used three-component microemulsions made from didodecyldimethylammonium bromide (DDAB), oil, and water. Rather than containing oil droplets as in oil-in-water microemulsions, these systems are bicontinuous and conductive over large regions of their phase diagrams (20). The bicontinuous structure features an extended, dynamic network of oil and water with DDAB residing at the interfaces.

Compared to oil-in-water microemulsions with solutes bound to relatively large oil droplets, mass transport is faster in the bicontinuous fluids. This is because nonpolar molecules travel in the oil phase and ions move along the water conduits in the oil-water networks of the fluid (18,21). Micellar media and microemulsions have been used previously to enhance the solubility of DDT for dehydrohalogenations (22).

In this paper, we report electrochemical and electrocatalytic reduction of DDT in a bicontinuous microemulsion. Electrolysis resulted in complete decomposition of DDT to less toxic homologues via loss of chlorine from aliphatic and aromatic positions. The fully dehalogenated 1,1-diphenylethane was obtained as one of the products of electrolysis.

EXPERIMENTAL

Chemicals and Solutions. *Tris*-(2,2'-bipyridyl)cobalt(II) perchlorate was synthesized as described previously (23). 2,2'-Bipyridine (Fisher) and dodecane (Janssen Chimica) were used as received. Didodecyldimethylammonium bromide, DDAB, (99+%, Eastman Kodak) was recrystallized from ethylacetate before use. 1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT, 98%, Aldrich) was recrystallized twice from hexane before use. 1,1-Dichloro-2,2-bis(4-chlorophenyl)ethene, DDE, was synthesized by published methods (9,24) and showed a single peak upon gas chromatographic analysis. Water was purified with a Sybron-Barnsted Nanopure water purification system.

Microemulsions were made by titrating a 2.7/1 mixture of dodecane and DDAB with water until a clear, conductive fluid was obtained (18). This mixture had a composition of 21/57/22 by weight DDAB/dodecane/water. After stirring for 24h, the bicontinuous microemulsion was stable at room temperature for at least a month. This fluid had specific conductivity 1.87 m Ω^{-1} cm⁻¹, and the addition of supporting electrolyte was unnecessary for electrolytic experiments.

Apparatus and procedures. An EG & G Princeton Applied Research Potentiostat/Galvanostat (Model 273) was used for cyclic voltammetry (CV). A three electrode single-compartment cell was used for electrochemical experiments and was thermostated at 25 or 30 °C. The working electrode was a glassy carbon disk (geometric $A = 0.071 \text{ cm}^2$), and the surface was prepared prior to each voltammetric scan by metallographic polishing with diamond paste, and then 0.3 and 0.05 μ m alumina (25). The counter electrode was a platinum wire and the reference electrode was a Ag/AgBr wire. Ohmic drop of the cell was electronically compensated in all experiments.

Solutions for voltammetry were usually 5-10 mM in DDT. Measurements were usually made after purging with purified nitrogen for 20 minutes.

Bulk electrolyses of DDT and DDE were carried out in the same cells as described above using carbon felt (type VDG, National Electrical Carbon Corp.) cathodes ($5.7 \times 1.0 \times 0.5$ cm). The counter electrode was a carbon rod and the reference electrode Ag/AgBr. The potential of the cell was controlled by an EG & G Princeton Applied Research Potentiostat/Galvanostat (Model 363).

Electrolyses were done with 10 mL microemulsion containing 10 mM DDT or DDE. $Co(bpy)_3^{2+}$ was 1 mM. In most electrolyses, purified nitrogen was bubbled through the solution 20 minutes before and during the reaction. To enhance mass transport, ultrasonication was applied with a Fisher Sonic Dismembrator (Model 300) by inserting a titanium microtip (Model 15-338-41) into the center of the cell set at 30% power. The temperature of the stirred solution was controlled at $30\pm2^{\circ}C$ and the reaction time was usually 3h.

After electrolysis the carbon felt was extracted with ultrasonication in CH₂Cl₂ (usually 8x) until the washing solution contained no more products as determined by thin layer chromatography. The extracts (50 mL) were combined with the microemulsion and filtered, the water phase from the microemulsion was pipetted off (ca. 1.5 mL), and nitrogen was bubbled through the solution to evaporate CH₂Cl₂ until DDAB began to precipitate. After storing this mixture (ca. 7 mL) in the refrigerator, DDAB precipitated, allowing its removal by filtration. This precipitate was separated and washed with cold CH₂Cl₂. It did not contain significant amounts of reaction products, as determined by GC-MS.

The resulting microemulsion extract was analyzed by GC-MS using a Hewlett-Packard 5890A Gas Chromatograph with a 5970 Series Mass Selective Detector and a Hewlett-Packard 12m x 0.2mm (0.33 μ m) methyl silicone column. Helium flow rate was 1 mL min⁻¹, and the initial oven temperature of 35 °C was increased at a rate of 5° C/min to the final temperature of 250 °C. Peaks attributed to DDT congeners were separated by GC and identified through comparison with literature MS data and by using a Hewlett-Packard Mass Spectral Data base (MSD) library. The spectra for aliphatic or aromatic chlorine compounds with identical molecular formulae were assigned by comparing retention times with those reported in the literature. UV-spectra were recorded with a Beckman DB-GT spectrophotometer.

RESULTS

Voltammetry. DDT, DDE, bipyridyl, oxygen and Co(bpy)3²⁺ were quite soluble in the DDAB/dodecane/water (21/57/22) microemulsion. Cyclic and square wave voltammetry were used to characterize direct and catalytic redox reactions. Voltammetric reduction of DDT in the microemulsion with no catalyst present revealed two peaks at about -1.4 V and -2.0 V (Figure 1). These peaks denote a flow of electrons to organic species in solution, presumably resulting in the cleavage of C-Cl bonds. No peaks were found on the reverse scans of the voltammograms, showing that the electrolytic reductions are irreversible. Similar results were found for DDT in N,N-dimethyformamide (DMF).

Voltammetry was also used to evaluate redox catalysis which might be used to lower the potential for DDT dechlorination. Tris-(2,2'-bipyridyl)cobalt(II) [Co(bpy)₃²⁺] was previously used to dechlorinate alkyl and aryl halides in aqueous solutions of cationic surfactants (26,27). When this catalyst was placed into the microemulsion with excess bipyridyl to retard dissociation of intermediate complexes, a reduction peak at about -0.9 V was observed accompanied by an oxidation peak on the reverse scan (Figure 2). This peak pattern is similar to that observed in micellar solutions of cetyltrimethylammonium bromide (CTAB) in water (23,26), and is assigned to the reversible Co(II)/Co(I) redox couple of the bipyridyl complex.

A second reduction peak was found at -1.05 V with no accompanying oxidation peak. This is very different from results in aqueous CTAB solutions, where a second peak is found in which $Co(I)(bpy)_3$ + accepts two electrons from the electrode, with a chemically reversible pair of oxidation-reduction peaks at a potential 0.3 V more negative than the first peak (23,26). In the microemulsion, the second reduction peak is irreversible, shifts to negative potentials as the rate of potential scanning is increased, and has a height smaller than the first one-electron reduction peak (Table 1).

CVs obtained after addition of DDT to microemulsions containing $Co(bpy)3^{2+}$ gave a large broad reduction peak at about -1 V (Figure 3). No oxidation peaks were observed. The height of the peak was increased about 20-30 fold over that of the catalyst alone (Table 2). The peak potential was shifted slightly negative of the first catalyst peak, but was about 0.4 V positive of the first peak for direct reduction of DDT (cf. Figure 1). This type of voltammetric behavior is characteristic of the catalytic dechlorination of organohalides (17a). The typical scenario is reaction of a reduced form of the catalyst with the organohalide. The current is increased because catalyst ions are regenerated at the electrode, in this case in the Co(II) form, to participate in further catalytic cycles. No oxidation peak is observed because the reduced form of the catalyst reacts with DDT.

Oxygen was estimated by CV to be about 7-fold more soluble in the microemulsion than in water, with an equilibrium concentration of about 9 mM. Although oxygen is usually removed from electrolytic solutions, we wished to see if we could detect any catalytic reactivity with DDT, as has been reported in organic solvents (16). Oxygen gave an irreversible peak at -0.5 V by square wave voltammetry (Fig. 4). A catalytic increase in the reduction current was observed at this low potential when DDT was added to the microemulsion. These results suggest catalysis involving reaction of a reduction product of oxygen and DDT.

Controlled Potential Electrolyses. Voltammetric results provided the basis for choosing the conditions for electrolysis of DDT under potential control using large carbon felt cathodes. Most electrolyses were run for three hours, using 10 mL of microemulsion and a variety of experimental conditions. Table 3 shows the percentage yields of products resulting from uncatalyzed or catalytic electrolysis of DDT as found by GC-MS. Peak integrations were done neglecting products not



Figure 1: Cyclic voltammogram on glassy carbon of 5 mM DDT in microemulsion at 60 mV s⁻¹. **Figure 2**: Cyclic voltammogram on glassy carbon of 0.5 mM Co(II)(bpy)3(ClO₄)₂ with 1.5 mM 2,2'bipyridyl in microemulsion at 60 mV s⁻¹.



Figure 3. Cyclic voltammogram on glassy carbon of 5 mM DDT + 0.5 mM Co(II)(bpy)₃(ClO₄)₂ with 1.5 mM 2,2'-bipyridyl in microemulsion at 60 mV s⁻¹.

Figure 4. Forward current square wave voltammograms in microemulsions at 5 Hz, 25 mV pulse height, 1 mV step height: (a) saturated with oxygen; (b) saturated with oxygen + 10 mM DDT.

Scan rate (mV s ⁻¹)	first peak	ς	second peak			
	$E_p (V,Ag/AgBr) I_p (\mu A)$		E _p (V,Ag/AgBr) I _p (μA			
200	-0.896	2.52	-1.085	1.83		
100	-0.883	2.19	-1.070	1.23		
80	-0.883	2.02	-1.068	1.04		
60	-0.880	1.36	-1.056	0.84		
40	-0.880	1.12	-1.055	0.71		
20	-0.870	0.94	-1.042	0.44		
10	-0.870	0.67	-1.043	0.30		

Table 1. Voltammetric results for $0.5 \text{ mM Co(II)(bpy)}_3(ClO_4)_2 + 1.5 \text{ mM bpy in a microemulsion of DDAB/dodecane/water}$

_	Scan rate (mV/s ⁻¹)	E _p (V, Ag/AgBr)	I _{cat} (μA)	I _{cat} /I _d a
	100	-1.025	46.5	21.2
	80	-0.993	50.0	24.8
	60	-0.9 9 2	40.0	29.4
	40	-0.992	31.2	27.9
	20	-0.978	19.5	20.8
	10	-0.969	14.4	21.5

Table 2. Catalytic efficiency for the reduction of 5 mM DDT by $0.5 \text{ mM Co}(\text{bpy})3^{2+} + 1.5 \text{ mM bpy}$ in a microemulsion of DDAB/dodecane/water

 $a_{I_{cat}}$ = catalytic peak current for DDT + catalyst present. I_d = peak current of catalyst alone.

containing characteristic signals of the diphenylethane structure, which included several decomposition products of the microemulsion components (19), such as undecane ($R_t = 13.0 \text{ min}$) and dimethyldodecyl amine ($R_t = 24.1 \text{ min}$).

Direct reduction at -1.4 V of 10 mM DDT resulted in 51% decomposition of the starting material with DDD and DDE as major products (Table 3a). No DDT remained after electrolysis at a potential of -2.0 V, and DDE and related substances were found as well as products of aliphatic and aromatic chlorine removal. The completely dehalogenated 1,1-diphenylethane was detected in 1% yield (Table 3b). Reduction of DDE at -2.3 V under the same conditions gave mainly the expected products of stepwise Cl loss of the ethene derivatives (Table 3c). In experiments where no nitrogen was passed through the solution, nearly all aliphatic and a large fraction of aromatic chlorines were removed, so that 1-(4-chlorophenyl)-1-phenylethane and 1,1-diphenylethane were obtained in the highest yields of all electrolyses (Table 3d).

The catalytic influence of $Co(bpy)3^{2+}$ was examined at -1 V (Table 3e). Compared to the uncatalyzed reduction at -1.4 V, a larger percentage of DDT was decomposed. Although in both electrolyses no aromatic chlorine loss was induced, 24% DDO was obtained in the presence of $Co(bpy)3^{2+}$ compared to 6% without this catalyst. When extending the reaction time from 3h to 8h (Table 3f), the yield of DDD and DDMS decreased, accompanied by an increased percentage of DDMU. At the relatively positive potential of -1 V the presence of oxygen in the reaction medium produced a small amount of aromatic dechlorination. The completely dechlorinated product was 2% of the product mixture, while 3% of the compound with one chlorinated benzene ring was found (Table 3g).

The color of the reaction mixture changes from yellow to red during electrolysis. UV-VIS spectroscopy of the red water phase which separates after methylene chloride extraction shows characteristic absorption peaks of $Co(bpy)_3^{2+}$ even after 8 h electrolyses. These results suggested that extensive decomposition of this catalyst did not occur.

											at., n
DDT 9)	!	0.3	54	7	21	I	4	13	e	2	V, Co ci
D0T †)	I	8	25	4	43	1	1	20	ŀ	I	hr; g) - I
e)	ω	17	24	12	17	1	I	24	1	I	o cat., 8
DDT d)	1	1	4	I	е	I	I	37	22	34	-1 V, C
р0Е с)	1	I	÷.	I	10	m	65	18	ъ	ł	0 cat. 1)
100 (q	I	-	5	27	9	m	I	55	N	-	<u>) - I V, C</u>
DDT a)	4 0	10	31	-	ო	I	I	ę	l	I	no N ₂ ; e
Ret.time (min.)	40.17	38.68	37.34	36.65	35.91	34.54	32.44	32.29	27.64	22.89	d) -2 V.
TS, % Abbr.	DDT	QQQ	DDE	SMOO	NMOQ			000)-2.3 V;
TABLE 3. ELECTROLYSIS RESUL Compound											Conditions: a) -1.4 V; b) -2 V; c

10 N₂.

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DISCUSSION

Carbon felt is environmentally acceptable and inexpensive and was an effective cathode for DDT electrolyses. The cell has a simple one-compartment batch reactor design.

Voltammetry showed that uncatalyzed electrolytic reduction of DDT on carbon cathodes requires a quite negative potential in the microemulsion and in organic solvent. Reduction takes place in at least two steps as shown by the two irreversible waves in CV (Fig. 1). Product yields (Table 3) indicate that removal of aliphatic chlorines begins at potentials of the first peak at -1.4 V. Further reduction of products of the initial chlorine removal and a small amount of reduction of aromatic chlorines occurred at -2V.

Tris-(2,2'-bipyridyl)cobalt(II) was a successful catalyst for dehalogenations in aqueous surfactant media, but tended to decompose during electrolyses (26). In the microemulsion, $Co(bpy)3^{2+}$ gave a reversible voltammograms for the Co(II)/Co(I) couple, and an irreversible second wave with a smaller current and less negative potential than expected for reversible reduction of $Co(bpy)3^{+}$.

After addition of DDT to the microemulsion containing $Co(bpy)3^{2+}$, cyclic voltammetry showed an increase in the Co(II) reduction peak and the disappearance of the anodic peak (Fig. 3). Currents about 20-30 times the height of the peak for the Co(II) reduction suggests a fast catalytic reaction of the electrogenerated Co(I) complex with the substrate DDT (17a). The catalytic reaction occurred 0.4 V less negative than the direct reduction of DDT.

Although oxygen was irreversibly reduced in the microemulsion, a slow catalytic reduction of DDT was found (Fig. 4), with approximately 0.9 V decrease in reduction voltage.

DDT was partly dechlorinated in 3 hour electrolyses without mediator (Table 3). As expected, aliphatic chlorines are the first removed. This resulted in DDE, DDD and DDO as major products. When applying the more negative potential of the second cathodic CV peak (Fig. 1), yields of DDMS and DDO increased. Also, about 1% of the completely dechlorinated 1,1-diphenylethane was found (Table 3b).

In order to get a better idea about the mechanism, pure DDE was electrolyzed under similar conditions (Table 3c). The major reaction product was 1,1-di(4-chlorophenyl)ethene. The appearance of products with the ethene structure after decompositions of DDT probably results from stepwise dechlorination of DDE rather than DDT. Possible reaction pathways are given in Figure 5.

Traces of di(4-chlorophenyl)acetaldehyde, which is a metabolite of DDT (28), were detected in several product mixtures. Molecular mass and fragmentation pattern confirmed this oxygenated species as the product of an unknown reaction mechanism.

Surprising results were achieved from electrolyses where oxygen was present (Table 3d). Aliphatic chlorines were removed yielding DDO (37%), 1-(4-chlorophenyl)-1-phenylethane (22%) and 1,1-diphenylethane (34%). The presence of O_2 during the electrolysis appears to enhance aromatic dehalogenation significantly. It is of interest that oxygen *does not* enhance reduction rates of 4,4'-dichlorobiphenyl (29), which has only aromatic chlorines. Since the catalysis by oxygen observed by voltammetry at -0.5 V (Fig. 4) probably involves the more easily removed aliphatic chlorines, it is possible that some activated intermediate formed in initial reactions facilitates the subsequent loss of aromatic chlorines. The mechanistic role of oxygen in these reactions is as yet unclear.

Electrolyses using -1 V and Co(bpy) 3^{2+} gave more extensive dechlorination (Table 3e-f) than electrolyses without catalyst at -1.4 V. Voltammetry suggests that Co(bpy) 3^{+} is the reactive species for aliphatic dechlorination. The presence of oxygen and Co(bpy) 3^{2+} at -1 V provided the largest

yields of DDE, as well as 3% 1-chlorophenyl(1-phenyl)ethane and 2% 1,1-diphenylethane. Again, the role of oxygen in these reaction is not fully understood.

CONCLUSIONS.

Methods described in this paper are capable of removing all chlorines from DDT under relatively mild conditions. The removal of both aliphatic and aromatic chlorines leads to quite complex intermediate reaction mixtures. Thus, results suggest that similar electrolysis methods can be used for a variety of different compound types. A similar method has been reported for the dehalogenation of mixtures of PCBs (19). Various possibilities for scale up and further optimization may lead to a feasible method to decontaminate toxic waste containing organohalides.

Microemulsions provide less expensive (30), less toxic reaction media than alternative organic solvents. These microheterogeneous fluids also tolerate the presence of water, with which organohalides are usually present in the environment. Microemulsions have good solubilizing properties, and can be used to remove pollutants from soils (31). The surfactant DDAB could be recovered during work-up, so that surfactant recycling appears feasible. The graphite felt cathode material is inexpensive and environmentally benign. Catalysis involving oxygen led to products with all aliphatic and one or both aromatic chlorines removed, and is therefore potentially attractive for applications.



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