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# Anodic Oxidation of DDT, Methoxychlor, and **Related Compounds**

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#### ABSTRACT

DDT, DDE, methoxychlor, and the ethylene of methoxychlor (MeCe) were oxidized in a 5% aqueous acetonitrile solution at a platinum electrode con-taining tetraethylammonium perchlorate or tetraethylammonium perfuoroborate as supporting electrolytes. The major electrolysis products were those which resulted from the hydrolysis of the electron-deficient intermediates and included alcohols, ketones, benzoquinones, and acids. 1,1-Bis-(p-methoxyphenyl) 2,2,2-trichloroethanol, not previously reported as a metabolic degrada-tion product of methoxychlor, was readily isolated as a major electrochemical oxidation product of both methoxychlor and MeCe.

No other man-made chemical has had more impact on the health of the human race or on the environment as has DDT. More than two million metric tons of DDT have been used for insect control since 1940. It has been estimated that DDT has saved fifty million human lives and spared one billion humans from such plagues as malaria, typhus, and yellow fever (1). DDT is considered to be the single major controllable factor that has led to the population explosion in underdeveloped nations of the world. Yet, due to its persistence in the environment, its ability to be "biologically magnified," and its ability to be rendered harmless by many strains of DDT-resistant insects, DDT has become the symbol of man's reckless environmental pollution (1). DDT or DDE, its more persistent degradation product, is found in virtually every environmental sample. DDT levels of from 1 to 10 ppm are generally observed in man. DDE has recently been recognized as the most abundant organochlorine pollutant in the environment.

In preliminary findings cited by Maugh (2), Moilanen and Crosby have shown that DDT undergoes rapid. vapor phase, sunlight degradation in air to DDE. DDE is in turn photodegraded much more slowly to at least eight other products, among them 4,4'-dichlorobenzophenone (DBP) and possibly to polychlorinated biphenyls (PCB's). Figure 1 shows the metabolic and photochemical degradation pathways of DDT involving oxidations. [A paper on the anodic oxidations of PCB's follows this paper (3)].

Effective on January 1, 1973, all use of DDT in the United States has been banned by the Environmental Protection Agency. Yet many agree that no single DDT substitute will be as inexpensive and as universally effective as was DDT. Methoxychlor, the methoxy analogue of DDT, has replaced DDT in certain commercial preparations as it has been found to be a persistent yet biodegradable insecticide. Metcalf has claimed that methoxychlor is one of the safest of all

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Fig. 1. Natural degradation pathways of DDT involving oxidations.  $h\nu$  denotes the proposed photochemical pathways in sunlight.

insecticides to higher animals (1). Figure 2 shows the known metabolic degradation pathways of methoxychlor (MeC) involving oxidations. Methoxychlor is metabolized through O-dealkylation to mono- and bisphenols, which are rapidly conjugated and excreted in higher animals or dehydrochlorinated to the corresponding ethylene (MeCe). Methoxychlor is more effective against DDT-resistant insects, such as the housefly, as the enzymatic-induced rate of dehydrochlorination of methoxychlor to the ethylene of methoxychlor (MeCe) is substantially reduced by the electron-donating properties of the p-methoxy groups in comparison to the over-all electron-withdrawing properties of the *p*-chloro groups of DDT.

It must be emphasized that the oxidative pathways occurring in this present report on the electrochemical Downloaded on 2013-11-28 to IP 35.8.11.2 address. Redistribution subject to ECS license or copyright; see ecsdl.org/site/terms\_use



Fig. 2. Degradation pathways of methoxychlor involving oxidations.

oxidation of DDT, methoxychlor, and related compounds are no doubt different than the enzyme-assisted, natural degradation routes of these same chemicals. It is interesting that 1.1-bis-(p-methoxyphenyl-2,2,2trichloroethanol, never before reported as a metabolic product of methoxychlor, is readily isolated as a major electrolysis product from the electrochemical oxidation of methoxychlor (MeC). All previous electrochemical studies of DDT and related compounds have been concerned with their electrochemical reduction (4-7). Lund has reported the electrochemical oxidation of 4.4'dichlorobenzhydrol (DCBH) at +2.07V vs. SCE in acetonitrile solvent to the ketone, 4.4'-dichlorobenzophenone (DBP) (8).

## Experimental

Chemicals.-The following chemicals were used as received after their purity had been checked by thinlayer or gas-liquid chromatography: 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane (DDT); 1,1-dichloro-2,2-bis-(p-chlorophenyl)ethylene (DDE); 1,1-bis-(pchlorophenyl)-2,2,2-trichloroethanol (Kelthane); 4,4'dichlorobenzophenone (DBP); 4,4'-dimethoxybenzo-phenone (DMBP); 1,1-dichloro-2,2-bis-(p-methoxyphenyl)ethylene (MeCe). 1,1,1-Trichloro-2,2-bis-(pmethoxyphenyl)ethane or methoxychlor (MeC) both purified and technical grade was kindly provided by the Biochemicals Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware. The technical grade was easily purified by recrystallization from ethanol. The following compounds were chemically prepared following published procedures: 4,4'-dichlorobenzilic acid (DBA) (9); 4,4'-dimethoxybenzilic acid or anisilic acid (DMBA) (10).

The following three compounds were isolated as major electrolysis products: 1,1-bis-(p-methoxyphenyl)-2,2,2-trichloroethanol or dimethoxykelthane (DMK) was isolated from the large-scale electrolyses of methoxychlor (MeC) and the ethylene of methoxychlor (MeCe); 1,1,1-trichloro-2-(p-methoxyphenyl)-2-(3chloro-4-methoxyphenyl)ethane (3-Cl-MeC) was isolated from the electrolysis of methoxychlor only anhydrous MeCN  $(0.1F LiClO_4)$  saturated in with Na<sub>2</sub>CO<sub>3</sub>; 1,1,1-trichloro-2-(p-chlorophenyl)-2-(4chloro-2,5-benzoquinone)ethane (DDT-Q) was isolated from the electrolysis of DDT, being the major product of the electrolysis of DDT in the flow-through cell. The physical as well as the spectroscopic data of these three new compounds have been reported elsewhere (11).

The acetonitrile solvent (MeCN) was purified by distillation from  $P_2O_5$  and then  $CaH_2$ , the middle 80% fraction being retained. Tetraethylammonium perchlo-

rate  $(Et_4NClO_4)$ , used as the supporting electrolyte, was recrystallized twice from distilled water, dried on top of an oven and in an evacuated drying pistol at  $100^{\circ}$ C with P<sub>2</sub>O<sub>5</sub> as dessicant. Tetraethylammonium fluoroborate  $(Et_4NBF_4)$  was prepared by reacting  $Et_4NBr$  with HBF<sub>4</sub>, followed by a washing with ether, two recrystallizations with ethanol and then one with distilled water. This supporting electrolyte was also dried on top of an oven and in an evacuated drying pistol. Due to the hazards of working with perchlorates, especially in the presence of heavy metals, the use of fluoroborate salts as supporting electrolytes was preferred in the latter portions of this work. Perhaps because all work was done in 5% aqueous acetonitrile there appeared to be little difference in the types or amounts of the products when Et<sub>4</sub>NBF<sub>4</sub> was used instead of Et<sub>4</sub>NClO<sub>4</sub>.

Conventional electrochemical equipment was used for the cyclic voltammetry (12, 13) and for the con-trolled potential electrolyses (Amel Model 557 potentiostat-galvanostat). Controlled potential coulometry was accomplished either by the deposit of silver onto a silver wire cathode (auxiliary electrode) or through a graphic integration of the current-time curve. For cyclic voltammetry, the electrolysis cell was a 4 oz glass jar; the working electrode was a stationary platinum disk (Beckman 39273); the auxiliary electrode was a platinum electrode placed coaxially around the working electrode; the reference electrode was an aqueous SCE isolated from the electrolysis by a two-compartment salt bridge to prevent contamination of the electrolysis cell by chloride. For controlled potential electrolyses, the electrolysis cell was a 250 ml beaker or a glass flow-through cell. With the beaker, the working electrode was a cylindrical platinum mesh electrode; the auxiliary electrode, isolated by a medium porosity glass frit, was either a coiled silver wire in a solution of 0.1F AgClO<sub>4</sub>-0.1F Et<sub>4</sub>NClO<sub>4</sub> or Et<sub>4</sub>NBF<sub>4</sub> in MeCN or a cylindrical platinum mesh electrode in 0.1F of the same supporting electrolyte as the working compartment; the reference electrode was a Ag/0.1F AgClO<sub>4</sub> in MeCN electrode. All potentials are given vs. the aqueous saturated calomel electrode (SCE); those measured against the Ag/AgClO<sub>4</sub> reference electrode were converted to the SCE reference electrode by adding +0.30V to the measured value (14).

In order to isolate a greater proportion of the primary hydroxylated product before it could be further oxidized at the electrode, a single-pass flow-through electrolysis cell was used; its construction out of glass being diagramed in Fig. 3. While the over-all product yield was between 10 to 30%, there were significantly fewer products with this flow-through cell. In addition, the unreacted 70-90% of the starting material was used over again in subsequent single-pass electrolyses. In general, while there might be ten or more products detected by thin-layer or high pressure liquid chromatography from a conventional electrolysis, usually only one to three products were observed when the same compound was electrolyzed in the single-pass flowthrough cell. It was not possible to make an exact mass balance as it was impossible to isolate in pure form nor to make satisfactory structure assignments to the many minor electrolysis products. As will be noted later, the product yields are low as they are based on the amount of pure isolated product after separation and purification. In most cases the electrolyses were run, exposed to the air, at the lowest controlled potential which produced significant current. The electrolysis was terminated when the current had reached a constant minimum value or when thin-layer chromatography indicated that all of the starting material had been consumed or interesting products were present. The solvent was removed by a rotary evaporator at temperatures below 50°C to minimize thermal degradation of unstable products. Procedures used for the isolation of various oxidation products were as follows: several extractions to isolate the neutral organic mate-

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Fig. 3. Single-pass, flow-through electrolysis cell. Of all glass construction, cell height 40 cm by 7.0 cm in maximum diameter. Made out of a 150 ml Filter funnel having a medium porosity glass frit, 5.5 cm in diameter (Corning 36060). WE, PT = working electrode, 100 mesh platinum, 5.5 cm in diameter, wire diameter 0.0076 cm; REF, SCE = reference electrode probe, ultra fine porosity, 0.5 cm in diameter located 1 cm above the working electrode; AUXIL = auxiliary compartment made of a medium porosity glass frit, 3.0 cm in diameter; CE, Pt = counterelectrode, 52 mesh platinum, 4.0 cm in height by 1.5 cm in diameter (not shown in the figure); AIR = coarse glass sparger to create a positive air pressure at the top of the cell, 1.5 cm in diameter; Dropping Funnel = dropping funnel, 100 ml graduated, ending in a 24/40 joint; VAC = provision to attach vacuum if needed to increase the flow rate.

rials from the acidic or phenol products, initial screening by thin-layer chromatography, open column chromatography to remove unwanted or long-eluting products, followed by either preparative thick-layer chromatography or semipreparative, high pressure, liquid chromatography. All of the chromatography was performed on the appropriate type of silica while the high pressure liquid chromatography-was performed on 6-12 ft by 7 mm ID packed columns of  $37-75\mu$  porous silica using a Waters ALC-201 chromatograph in the recycle mode with an all purpose refractive index detector. Visualization of products on TLC plates was accomplished by ultraviolet radiation or by one of the following spray reagents: concentrated sulfuric acid for DBA and many of the analogues of methoxychlor; diphenylamine-zinc chloride for Kelthane and dimethoxykelthane, 2,4-dinitrophenylhydrazine for the ketones and benzoquinones.

Product identifications were based on melting points compared to authentic samples, elemental analysis, infrared, nuclear magnetic resonance, and mass spectral Developed on 2013 11 28 to IP 25 8 11 2 address. Redistribution data (11). Mass spectra were obtained on an AEI MS-902 mass spectrometer with a resolution of 100,000.

## **Results and Discussion**

Cyclic voltammetry was initially used to determine the approximate potential at which to run the ensuing controlled potential electrolyses. Table I shows the anodic peak potentials for DDT, methoxychlor, and their related compounds. The diagnostic criteria of Nicholson and Shain (15, 16) were used to aid in suggesting the over-all major voltammetric anodic pathway of DDT, DDE, methoxychlor, and the ethylene of methoxychlor.

No signs of an electrochemical reversible couple (up to scan rates of 200 V/sec) were evident for any of the compounds listed in Table I except for a quasi-reversible peak for the ethylene of methoxychlor (MeCE) at scan rates greater than 1.0 V/sec. In general, the primary oxidation peak for DDT, DDE, MeC, and MeCE tended to shift to higher anodic potentials and the current function tended to decrease as the sweep rate was increased over four decades (0.01-100 V/sec). These behavior patterns are suggestive of an electron transfer followed by a fast irreversible chemical reaction [case VI of Ref. (15)] or an ECE pathway [either case I-I or I-R of Ref. (16)] with the second electron transfer being at the same or lower potential than the first electron transfer.

Referring to Table I, the presence of additional peaks at higher anodic potentials were due to the subsequent oxidation of the major electrolysis product, the corresponding benzophenone. Thus, the anodic peak at +2.65V for dichlorobenzophenone (DBP) is readily apparent in the anodic voltammograms of DDT, DDE, Kelthane, and DBA. Similarly the two anodic peaks of DMBP at +1.94 and +2.60V are observed in the anodic voltammograms of MeCE and DMBA and partially in the voltammograms of MeC and DMK.

As the controlled potential electrolyses of DDT and its related compounds proceeded very slowly in anhydrous MeCN, and in an effort to more nearly match natural oxidative degradation conditions, all electrolyses were run with water added to the acetonitrile solvent in an atmosphere of air. The weight of the AgCl precipitated in the anode compartment during the course of an oxidation indicated that an irreproducible amount of chloride was being lost from the a-chloromethyl group of each compound. Chromatographies indicated a multitude of electrolysis products, often between ten to twenty; some of them being heat or light sensitive. Hence the isolation and characterization of only the more abundant electrolysis products was possible. The reported product yields are low as they are based on the amount of pure isolated product obtained after separation and purification remembering in certain cases that incomplete controlled potential elec-trolyses were carried out in the single-pass flowthrough cell or in order to isolate the initial electrolysis product.

Electrochemical oxidation of DDE.—When DDE was electrochemically oxidized in 5% aqueous acetonitrile

Table I. Summary of anodic peak potentials of DDT, methoxychlor, and related compounds at 100 mV/sec vs. aqueous SCE

Compound	$E_{\nu}$ , V vs. SCE
DBP DMBP DBA DMBA Kelthane DMK DDE MeCE DDT MeC	+2.65 +1.94, +2.60 +2.21, +2.6 +1.57, +1.94, +2.60 +2.34, +2.66 +1.72, +1.88 +1.88, +2.75, (+2.15 to +2.30)* +1.54, +1.92, +2.60, (+1.57)* +2.32, +2.6

 $\ast$  An additional wave appearing only at scan rates of 2.5 V/sec or higher.

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at +1.74V on a platinum electrode, the major products isolated were DBA in 10-60% yield and DBP in 30-80% yield. The variable yield of DBA can, in part, be explained by the fact that DBA itself is slowly oxidized at +1.74V to DBP. At +2.00V in 5% aqueous MeCN, DDE, in about  $10^{-2}$  F, is electrochemically oxidized to DBP in greater than 95% yield in 3-5 hr as opposed to an average electrolysis time of 20 hr at +1.74V. At the higher controlled voltage of 2.00V, any DBA that may have been initially formed upon electrolysis of DDE, is itself quantitatively oxidized to DBP.

The isolation of DBA from the electrolysis of DDE, along with the cyclic voltammetric data, suggests that DDE may be electrochemically oxidized in an ECE pathway proceeding through an unstable vicinal-glycol (I); this very unstable intermediate would undergo rapid hydrolysis and dehydrochlorination to DBA, or could undergo the loss of the good leaving group, dichloromethylene (CCl<sub>2</sub>), to produce the benzophenone DBP. This oxidation of the vicinal-glycol (I) is analogous to the oxidation of benzophenone (17).

The fact that DBA at 1.74V is oxidized after 20 hr to DBP in only 20% yield (the remaining 80% being the starting material) and the highly irreproducible yields of DBP obtained in the oxidation of DDE at +1.74V, yet the consistent controlled potential coulometry indicating an over-all two-electron oxidation of DDE, suggest a branching pathway to the formation of DBP. Figure 4 depicts such a branching mechanism whereby the hydroxylated cationic species (II) or the vicinalglycol (I) undergo a purely chemical breakdown to DBP. Such a purely chemical pathway must be a significant alternative, as the oxidation of DDE through DBA to DBP requires the loss of four electrons, not the two that is consistently observed in the coulometry.

An additional anodic voltammetric wave for DDE at approximately +2.2V is apparent at scan rates of 2.5 V/sec or higher. This suggests that a branching reactions sequence occurs that is dependent on the rate of the voltage scan. At slow voltammetric scan rates, an initial over-all two-electron oxidation occurs as depicted by the top line of Fig. 4, while at faster scan rates a stepwise EEC sequence occurs as shown on the left-hand part of Fig. 4. This branching sequence is suggested by a significant increase (within bounds) of the current for the new peak at +2.15V with increasing scan rate.

Electrochemical oxidation of 1,1-dichloro-2,2-bis-(pmethoxyphenyl)-ethylene.—When MeCe was electrochemically oxidized in 5% aqueous MeCN at +1.40V on a platinum electrode, the major products were DMBP in 32-43% yield and the unexpected DMK in 25% yield. While DBA was a major product of the electrochemical oxidation of DDE at lower controlled potential, thinlayer chromatography indicated that no 4,4-dimethoxybenzilic acid (DMBA) was obtained in the electrochemical oxidation of MeCE. The closeness in the anodic peak potentials between MeCE and DMBA, within 0.03V (Table I), indicates that a significant accumulation of DMBA is not to be expected in the controlled potential electrolysis of MeCE. This is in sharp contrast to the 0.23V difference in anodic peak potentials between DDE and DBA, which permitted DBA to be isolated in significant amounts from the large-scale controlled potential electrolysis of DDE.

The isolation of DMK in 25% yield from the electrolysis of MeCE indicated that free chloride in the solution is capable of nucleophilic attack on the deficient intermediates to yield a tri-chloromethyl moiety. As MeCE exhibited cyclic voltammetric behavior similar to DDE, including the appearance of an additional anodic wave at +1.57V at faster scan rates, a branching mechanism similar to that proposed for DDE is proposed for MeCE and is depicted in Fig. 5.

Electrochemical oxidation of DDT.-When DDT was electrochemically oxidized in 5% aqueous MeCN at +2.10V on a platinum electrode, the products identified were DBP in an approximate yield of 25% and 1,1,1-trichloro-2-(p-chlorophenyl)-2-(4-chloroand 2,5-benzoquinone)ethane (DDT-Q) in 10% yield and Kelthane (indicated by thin-layer chromatography and spray tests); however the isolation of the Kelthane was not possible due to the extremely small amount present. The isolation of a significant amount of Kelthane from the large-scale, conventional anodic oxidation of DDT was not expected as the oxidation peak of Kelthane occurs within 0.02V of the one for DDT (Table I). The use of a flow-through cell designed to enable the initial hydroxylated product to be swept away from the electrode before it could suffer further oxidation failed to produce Kelthane. Instead the sole product isolated from the flow-through electrolysis of DDT was DDT-Q.

Cyclic voltammetric data at all scan rates indicated that DDT is oxidized irreversibly followed at higher anodic potential by the prominent oxidation peak for DBP. While a stepwise ECE reaction sequences could be written, a more general over-all two-electron branching scheme is depicted in Fig. 6 to account for the formation of the major products. Thus a nucleophilic attack by water on the dicarbonium ion (III) at the central  $\alpha$ -carbon would result in the formation of Kelthane and DBP while a nucleophilic attack by water on the electron-deficient aromatic ring would lead to DDT-Q.



Fig. 4. Electrochemical oxidation of DDE in 5% aqueous acetonitrile at +1.74V vs. SCE on a platinum electrode.









Fig. 6. Electrochemical oxidation of DDT in 5% aqueous acetonitrile at +2.10V vs. SCE on a platinum electrode.

Electrochemical oxidation of methoxychlor.--When methoxychlor (MeC) was electrochemically oxidized in 5% aqueous MeCN at  $\pm 1.50\,V$  on a platinum electrode, the products identified were DMBP in an approximate yield of 35% and dimethoxykelthane (DMK) in 5-30% yield. This is the first report of the isolation and identification of DMK as a degradation product of MeC.

In dry MeCN (0.1F LiClO<sub>4</sub> as supporting electrolyte) saturated with Na<sub>2</sub>CO<sub>3</sub>, the major electrolysis product of MeC was found to be 1,1,1-trichloro-2-(p-methoxyphenyl)-2-(3-chloro-4-methoxyphenyl)ethane (3-Cl-MeC) in 20% yield. The production of this chloro-adduct must occur as a result of the nucleophilic attack by chloride ion which is produced by the previous degradation of a trichloromethyl group of another methoxychlor molecule. 3-Cl-MeC was not observed by thinbawaroaber material bar a benzo-bawaroaber material bar a benzo-

of methoxychlor was carried out in 5% aqueous acetonitrile.

The cyclic voltammetric data and product isolation suggest that methoxychlor is oxidized in a general over-all two-electron scheme in aqueous MeCN as shown in Fig. 7. There was no significant evidence for the production of phenols or of their subsequent oxidation products, the benzoquinones. These products would indicate that a nucleophilic attack by water on the electron-deficient aromatic rings does not significantly occur in electrochemical oxidation. O-dealkylation of the methoxy groups to yield mono- or bis-phenols are the major, known natural degradation pathways of methoxychlor (Fig. 2). Electrochemical oxidation of either 2- or 4-methoxyphenol involving the hydrolysis of the carbonium ion and the loss of methanol to yield the benzoquinone has been reported (18, 19). Appar-



Fig. 7. Electrochemical oxidation of methoxychlor in 5% aqueous acetonitrile at +1.50V vs. SCE on a platinum electrode.

quinone with dealkylation is not a significant electrochemical oxidation pathway for methoxychlor in 5% aqueous acetonitrile at +1.50V.

#### Summary

The major electrolysis products identified from the controlled potential electrolyses of DDT, DDE, methoxychlor, and the ethylene of methoxychlor in 5%aqueous acetonitrile solution were hydrolysis products. These products were either alcohols, ketones, benzoquinones, or acids that suggested that nucleophilic attack by water occurred mostly at the electrondeficient carbon located at the central  $\alpha$ -carbon of each compound studied. The appearance at higher oxidation potential of a voltammetric wave of the benzophenone for each compound studied attests to this fact. DBA is obtained in good yield from the electrochemical oxidation of DDE, and the never-before reported DMK is obtained in good yield from the electrochemical oxidation of methoxychlor and the ethylene of methoxychlor, MeCe. However, nucleophilic attack by water on the electron-deficient aromatic ring did occur in certain cases as a significant amount of DDT-Q was isolated from the electrochemical oxidation of DDT. In an anhydrous media, a nucleophilic attack by chloride ion onto the electron deficient aromatic ring of methoxychlor was evident.

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