Voltammetric Identification of Organochlorine Insecticides, Polychlorinated Biphenyls, Polychlorinated Naphthalenes and Polychlorinated Benzenes[1, 2]

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INTRODUCTION

The chromatographic procedures normally used for the analysis of chlorinated hydrocarbons in the environment, e.g., gas-liquid chromatography and thin-layer chromatography, are limited by the fact that the analytical information obtained by any one method is generally insufficient to warrant more than tentative identification. This ambiguity arises due to the failure to establish a set of distinctive properties which could serve as a "fingerprint" for each compound. Infrared spectra provide such "fingerprinting", but most samples obtained from the environment are too small to be identified by infrared spectrometry. Gas-liquid chromatography-mass spectrometry (GLC-MS) can be employed as a method for classification, but it does not establish identification in all cases. For example, the mass spectra of the isomeric polychlorinated biphenyl compounds can be used to determine the number of chlorines on each biphenyl, but it cannot distinguish between the different isomers (SAFE and HUTZINGER 1972). One approach toward the identification of certain organochlorine insecticides by means of a characteristic fingerprint has recently been reported using UV-induced degradation patterns (KAUFMAN et al. 1972).

A study of the voltammetric reduction of various chlorinated compounds was initiated in order to investigate the possibility of a voltammetric detector for chlorinated hydrocarbons in the environment. This detector could provide both gross classification, such as distinguishing between polychlorinated biphenyls (PCB) and polychlorinated naphthalenes (PCN), and identification of the specific isomer in each class of compound. Normal dc polarography of certain organochlorine insecticides has previously been reported in the literature (ROSENTHAL et al. 1957, KEMULA 1967), but our paper reports the first voltammetric reduction of the PCB's and PCN's. The reduction potential data are presented in this paper as a preliminary description of the analytical methodology applicable to the rapid identification of these compounds. Although some of the compounds

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investigated are unlikely environmental pollutants, they were investigated as part of a systematic study of the voltammetric detector principle.

EXPERIMENTAL

Asymmetric PCB isomers, with chlorines on one ring, were synthesized from the appropriate chloroaniline by the Gomberg reaction using basically the method of WEINGARTEN (1961). The symmetric PCB's were prepared by the tetrazotization of the appropriate chlorinated benzidine followed by acidic decomposition of the tetrazonium salt with H_3PO_2 or CuCl/HCl. Monoacetylation of 2,5,2',5'-tetrachlorobenzidine allowed for the synthesis of 2,5,2', 4',5'-pentachlorobiphenyl. Specifically, 2,5,2',5'-tetrachlorobenzidine was monoacetylated with acetic anhydride. The resulting compound was diazotized, added to CuCl/HCl to yield 2,5,2',4',5'-pentachloro-N-acetyl-4-aminobiphenyl. This product was deacetylated in H_2SO_4, diazotized and added to H_3PO_2 giving 2,5,2',4',5'-pentachlorobiphenyl. All the PCB's prepared were confirmed by mass spectrometry and melting points. The purity of each compound was shown to be at least 95% by GLC.

The organochlorine pesticides and the chlorobenzenes were obtained from commercial sources. The PCN's were generous gifts from Dr. Julius Hyman, Berkeley, California; Imperial Chemical Industries, Ltd., England; and Dr. Dusan Hadzi and Dr. Ludvik Cencelj, Univ. Institute of Boris Kidrie, Ljubljana, Yugoslavia.

The apparatus used for this study employed three-electrode potentiostatic control circuitry with interruptable linear voltage sweep control. The logic-controlled interrupted voltage scan was used to minimize interference due to preceeding reduction steps in polychlorinated compounds (FARWELL et al., in preparation). The normal voltage scan rate was 142 millivolts/sec.

The reference electrode was an aqueous saturated calomel electrode (SCE), the auxiliary electrode was a platinum wire, and the stationary working electrode was a mercury-coated platinum electrode with an area of 42 mm^2. The sample cell volume was 3 ml. All solution concentrations were 5×10^{-4} $\underline{M}$ in the electroactive species. Dimethyl sulfoxide was used as the solvent with 0.1 $\underline{M}$ tetraethylammonium bromide (Et_4NBr) as the supporting electrolyte. Nitrogen gas was used for deaeration.

RESULTS

Figure 1 shows the reduction voltammograms for 1,3,5,7-tetrachloronaphthalene. Figure 1-A is the normal single-sweep oscillographic voltammogram and Figure 1-B is the second derivative voltammogram of 1-A. In order to significantly improve the quantitative resolution for the individual peaks, a temporary interruption of the linear voltage sweep at each wave was necessary. The analog second derivative of the current was used to control the voltages at which the scans were interrupted (E_{2d} values). Thus, the interrupt or hold potential and the length of the hold were automatically controlled by the voltammetric instrument. Figure 1-C demonstrates the interrupted-sweep or sequential ramp-and—hold oscillographic voltammogram.

Figure 2 shows the ramp-and-hold voltammograms for hexachlorobenzene, DDE and 2,4,5,2',4',5'-PCB. These current-voltage curves demonstrate that pure unknowns can be identified by visual comparison with known voltammograms. Both the relative reduction potentials and the relative intensities for the reduction peaks are useful in visual identification. In addition to the ramp-and-hold fingerprint, the normal single-sweep and second derivative oscillograms are available for identification of unknowns.

Tables 1,2,3 and 4 present the E_{2d} and the ΔE_{2d} for organochlorine pesticides, PCB's, PCN's and the polychlorinated benzenes. The E_{2d} values were obtained from a digital voltage read-out of the interrupted or hold potentials. The E_{2d} value is an "apparent" half peak potential $E_{p/2}$ since the E_{2d} voltage is determined by the second derivative crossing zero. The compounds which appear in Tables 1-4 are representative of approximately 100 organochlorine compounds that have been analyzed in our research.

DISCUSSION

As evident from Figures 1 and 2 and Tables 1-4, the reduction fingerprints and/or E_{2d} values are distinctive for the individual chlorinated compounds. While the apparent E_{2d} values have been shown to vary by as much as 20 millivolts from day to day under our experimental conditions, each reduction peak shifts by the same amount for a particular compound; therefore, the relative difference in millivolts between the individual reduction peak (reported as ΔE_{2d}) is constant. Consequently the data for the PCB's can be corrected to an internal standard value which is the biphenyl E_{2d} reduction potential (arbitrarily set at -2.411 V). Likewise the data for the PCN's can be compared to an internal standard which is the second reduction wave for naphthalene (arbitrarily set at -2.326 V). Data gathered on any one day has been shown to be reproducible to within ± 2 millivolts.

Since the voltammetric detector requires relatively pure compounds for positive identification, it will have to be connected to a chromatograph (GLC or LC) in order to analyze complex mixtures (MAIRANOVSKII and YANOTOVSKII 1963; KOEN et al. 1970). In cases where two components have the same retention time, the voltammogram for the chromatographic peak would contain additional waves and warn the analyst that the anticipated compound is contaminated.

A detection limit of 2×10^{-9} $\underline{M}$ has been reported for a polarographic detector which employed a carbon membrane electrode (PUNGOR and SZEPESVARY 1968). A microcell with a detector volume of 20 μl should provide a sensitivity of about 20 ppb.

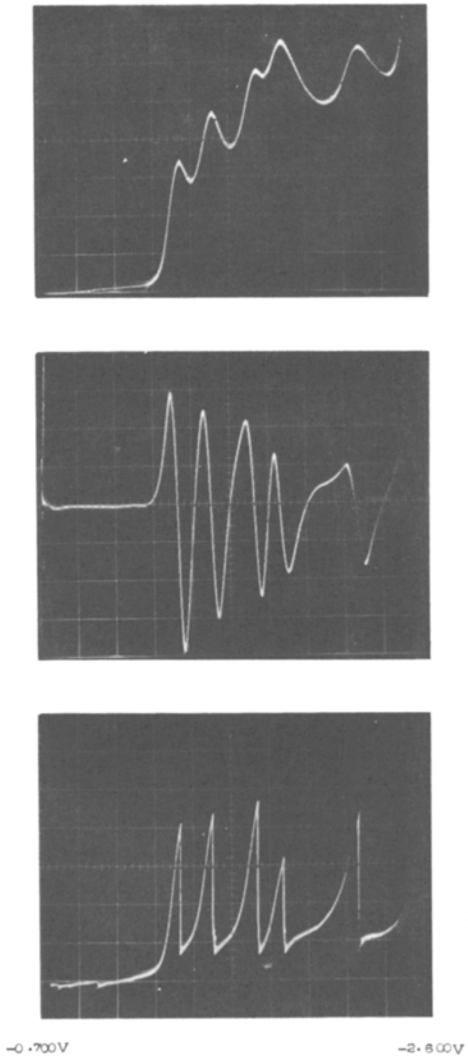

Figure 1: Reduction of 1,3,5,7-PCN
A: Normal voltammogram
B: Second derivative voltammogram
C: Interrupted scan voltammogram

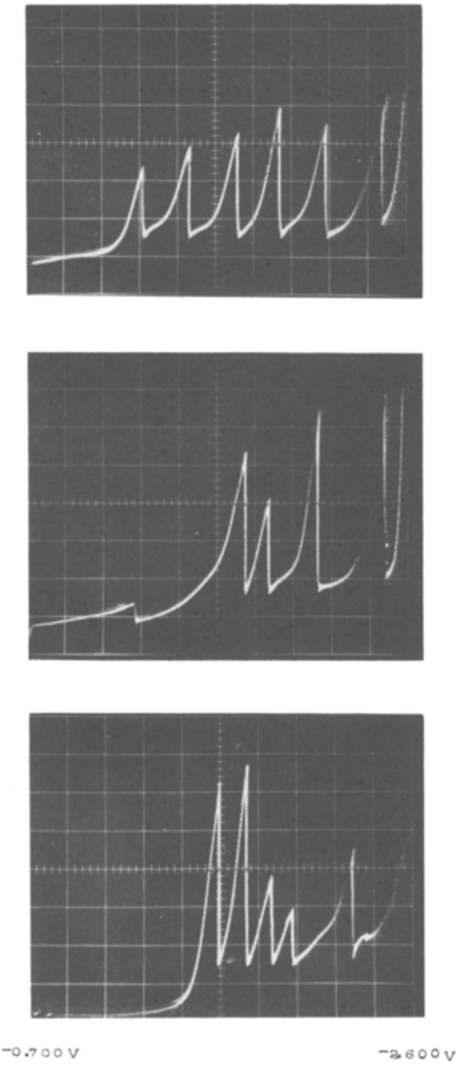

Figure 2: Interrupted scan voltammograms
A: Hexachlorobenzene
B: DDE
C: 2,4,5,2',4',5'-PCB

TABLE 1

Reduction Potentials of Selected Organochlorine Insecticides

Sample	E_{2d} in volts	ΔE_{2d} in volts
Heptachlor	-1.656 -2.087 -2.319	-0.431 -0.232
Dieldrin	-1.675 -2.038 -2.233 -2.450	-0.363 -0.195 -0.217
DDE	-1.814 -1.935 -2.177 -2.506	-0.121 -0.242 -0.329
Aldrin	-1.716 -2.055 -2.248 -2.453	-0.339 -0.193 -0.205
Lindane	-1.521 -2.006 -2.281	-0.485 -0.275
Chlordene	-1.753 -2.106 -2.333	-0.353 -0.227
trans-Chlordane	-1.565 -1.951 -2.172 -2.387	-0.386 -0.221 -0.215

TABLE 2

Reduction Potentials of Selected PCB's

Sample	E_{2d} in volts	ΔE_{2d} in volts
Biphenyl	-2.411	
2-	-2.101 -2.411	-0.310
2,5-	-1.944 -2.100 -2.411	-0.156 -0.311

TABLE 2 (cont.)

Sample	E_{2d} in volts	ΔE_{2d} in volts
2,6-	-2.108	-0.303
	-2.411	
2,4,5-	-1.837	-0.118
	-1.955	-0.151
	-2.106	-0.305
	-2.411	
3,4,5-	-1.696	-0.198
	-1.894	-0.198
	-2.092	-0.319
	-2.411	
2,3,5,6-	-1.787	-0.117
	-1.904	-0.194
	-2.098	-0.313
	-2.411	
2,3,4,5,6-	-1.552	-0.228
	-1.780	-0.131
	-1.911	-0.179
	-2.090	-0.321
	-2.411	
2,2'-	-2.126	-0.285
	-2.411	
4,4'-	-2.000	-0.411
	-2.411	
3,3'-	-2.030	-0.098
	-2.128	-0.283
	-2.411	
2,4'-	-2.042	-0.369
	-2.411	
3,4,3',4'-	-1.764	-0.239
	-2.003	-0.109
	-2.112	-0.299
	-2.411	
3,5,3',5'-	-1.720	-0.087
	-1.807	-0.181
	-1.988	-0.115
	-2.103	-0.308
	-2.411	

TABLE 2 (cont.)

Sample	E_{2d} in volts	ΔE_{2d} in volts
2,5,2',5'-	-1.901 -2.017 -2.120 -2.411	-0.116 -0.103 -0.291
2,6,2',6'-	-2.123 -2.411	-0.288
2,5,2',4',5'-	-1.771 -1.871 -1.981 -2.093 -2.411	-0.100 -0.110 -0.112 -0.318
2,4,5,2',4',5'-	-1.764 -1.902 -2.023 -2.127 -2.411	-0.138 -0.121 -0.104 -0.284
2,4,6,2',4',6'-	-1.908 -2.047 -2.411	-0.139 -0.364

TABLE 3

Reduction Potentials of Selected PCN's

Sample	E_{2d} in volts	ΔE_{2d} in volts
Naphthalene	-2.199 -2.326	-0.127
1-	-1.939 -2.326	-0.387
2-	-1.975 -2.326	-0.351
1,2,3-	-1.559 -1.766 -1.977 -2.326	-0.207 -0.211 -0.349

TABLE 3 (cont.)

Sample	E_{2d} in volts	ΔE_{2d} in volts
1,2,3,4-	-1.393	-0.170
	-1.563	-0.188
	-1.751	-0.195
	-1.946	-0.380
	-2.326	
1,2,3,5-	-1.411	-0.180
	-1.591	-0.193
	-1.784	-0.164
	-1.948	-0.378
	-2.326	
1,3,5,7-	-1.444	-0.171
	-1.615	-0.221
	-1.836	-0.124
	-1.960	-0.366
	-2.326	
1,3,5,8-	-1.373	-0.243
	-1.616	-0.167
	-1.783	-0.163
	-1.946	-0.380
	-2.326	
1,2,3,5,7-	-1.342	-0.168
	-1.510	-0.130
	-1.640	-0.195
	-1.835	-0.149
	-1.984	-0.342
	-2.326	

TABLE 4

Reduction Potentials of Selected Polychlorinated Benezenes

Sample	E_{2d} in volts	ΔE_{2d} in volts
Benzene	no reduction	
1-	-2.440	
1,2-	-2.217	-0.223
	-2.440	
1,4-	-2.198	-0.242
	-2.440	
1,2,3-	-1.962	-0.244
	-2.206	-0.234
	-2.440	

TABLE 4 (cont.)

Sample	E_{2d} in volts	ΔE_{2d} in volts
1,2,4-	-1.997 -2.200 -2.440	-0.203 -0.240
1,2,3,4-	-1.764 -2.000 -2.201 -2.440	-0.236 -0.201 -0.239
1,2,4,5-	-1.808 -1.997 -2.201 -2.440	-0.189 -0.204 -0.239
1,2,3,4,5-	-1.573 -1.802 -2.003 -2.201 -2.440	-0.229 -0.201 -0.198 -0.239
1,2,3,4,5,6-	-1.321 -1.565 -1.799 -1.996 -2.201 -2.440	-0.244 -0.234 -0.197 -0.205 -0.239

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