Electrochemical Reduction of DBDT at a HMDE

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The electrochemical cleavage of carbon-chlorine bond in DBDT has been studied using cyclic voltammetric, chronoamperometric and chronopotentiometric techniques. The transfer and diffusion coefficients of the species are evaluated from the data obtained and the mechanism of the reduction process is discussed.

The electrochemical reduction of gem-halides takes place in stepwise manner. Generally, the reduction of first C-X bond is easier than the remaining C-X bonds - C-F_3 being an exception. Literature survey revealed the use of polarographic technique to study the gem-halogenated insecticides [1]. Macro electrolysis at controlled potentials has been attempted to study the degradation products [2]. The present study on the electrochemical reduction of 1,1,1-trichloro-2,2-bis(p-bromophenyl)-ethane (DBDT) is an attempt to get an insight into the electrochemical reduction mechanism of carbon chlorine bond, using cyclic voltammetric, chronoamperometric and chronopotentiometric techniques. The theoretical principles and various applications of the voltammetric techniques have been described in detail in the literature [3,4].

MATERIALS AND METHODS

1,1,1-Trichloro-2,2-bis(p-bromophenyl)-ethane (DBDT) was prepared by condensing chloral hydrate with bromobenzone. The procedure adopted was same as for the preparation of DDT [5]. The m.p was 138-139°C.

The four different supporting electrolytes used were

(A) 0.1M tetraethylammoniuum bromide (TEAB) in 75% ethanol

(B) 0.1M TEAB in 50% isopropanol

(C) 0.05M TEAB in 50% DMF

(D) 0.02M tetrabutyl-ammonium iodide (TBAI) in 75% ethanol.

Aqueous ethanol media were prepared starting from absolute ethanol. Other chemicals used were of B.D.H. Analar grade.

The details of the instrument employed and the experimental procedure have been reported earlier [6,7].

RESULTS AND DISCUSSION

Cyclic Voltammetric Results

Cyclic voltammograms of DBDT follow the same pattern in all the media studied. Peak potential values for the electrochemical reduction process of carbon-chlorine bond in DBDT in various media at differrent sweep rates are presented in Table 1.

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Table 1

Cyclic Voltametric Results of DBDT

Different Supporting Electrolytes & Different Scan rates (v in V/sec)

v V/sec	$-E_p$ (V)	i_p (μA)
(A) 0.1 M TEAB in 75% EtOH; DBDT = 1 mM		
0.01	0.79	1.2
0.02	0.80	2.2
0.04	0.86	3.4
0.10	0.90	5.2
0.20	0.92	9.6
(B) 0.1M TEAB in 50% I-PrOH; DBDT = 0.5 mM		
0.01	-	0.60
0.025	0.80	1.0
0.05	0.80	1.2
0.10	0.85	1.6
0.25	0.87	2.6
0.50	0.95	3.5
(C) 0.05M TEAB in 50% DMF; DBDT = 0.25 mM		
0.05	0.90	0.5
0.10	0.825	1.1
0.25	0.80	2.0
0.50	0.825	3.0
(D) 0.02M TBAI in 75% EtOH; DBDT =0.5 mM		
0.01	0.90	0.7
0.025	0.95	1.2
0.05	1.00	1.8
0.10	1.00	3.0

It can be noted that the peak potential in 75% EtOH shifts in the negative direction with change from 0.1 M TEAB to 0.02 M TBAI. This is attributed to the size of the tetraalkylammonium cation used [7]. The plots betwen i_p *vs* $v^{1/2}$ are linear in all the media studied (Fig. 1). This showed that the reduction process is diffusion controlled.

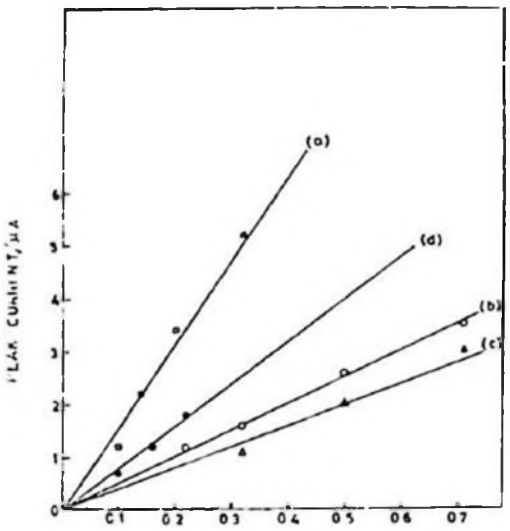


Fig. 1 i_p *vs* $v^{1/2}$ Plots of DBDT
(A) 0.1M TEAB in 75% ethanol
(B) 0.1M TEAB in 50% isopropanol
(C) 0.05M TEAB in 50% DMF
(D) 0.02M TBAI in 75% ethanol.

Variation of peak potential with sweep rate suggests the electrochemical reduction of DBDT is irreversible. This is confirmed by the absence of anodic peak in the reverse scan in all the media studied. Well defined peaks have been noticed in 0.05 M TEAB in 50% DMF. But the values of $i_p/v^{1/2}C$ in propanol and DMF are lower (Table 2) because of higher viscosity.

The slope of E_p log v plot gives the value of αn_a. Diffusion coefficent of DBDT is taken to be similar to that of DDT. The latter has been evaluated from chronopotentiometric data and reported as $D = 3.27 \times 10^{-6}$ cm^2 sec^{-1} in 0.1M TEAB in 75% ethanol [9]. Using αn_a and D, the value of $i_p/v^{1/2}C$ is evaluated. Comparing this with experimental value (Table 2) indicates the value of n as 2 in all media.

Table 2

Cyclic Voltammetric Data

n V/sec	[DBDT] mM	i μA	$i_p/v^{1/2}C$
0.1M TEAB in 75% ethanol			
0.20	1.00	9.6	21.50
0.04	0.40	1.8	22.50
0.1M TEAB in 50% isopropanol			
0.01	0.50	0.6	12.00
0.05M TEAB in 50% DMF			
0.10	0.25	1.1	13.91
0.10	0.20	0.8	12.65
0.02M TBAI in 75% ethanol			
0.10	0.50	3.0	18.97
0.025	0.50	1.2	15.20

Chrono amperometric (current-time) curves were recorded in all media using step potentials on the diffusion limited region of the corresponding cyclic voltammograms for the compound. The $it^{1/2}$ vs t plots (Fig.2) are generally horizontal showing the electrochemical reduction process to be purely diffusion controlled.

Typical chronopotentiograms are (Fig.3) well defined in all media except in 0.02M TBAI in 75% ethanol medium. $it^{1/2}$ values of DBDT at different applied current densites are found to be constant. This confirms that

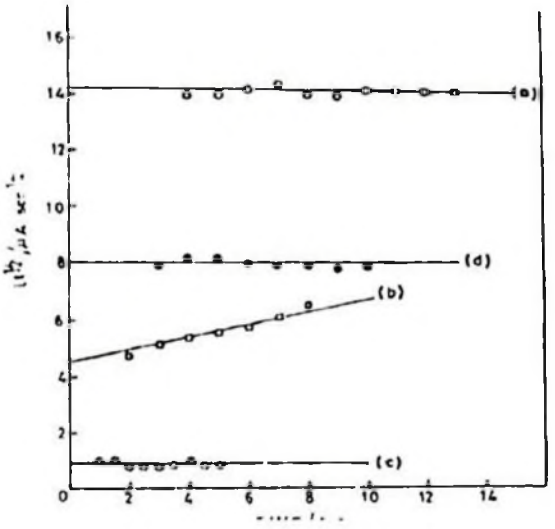


Fig. 2 $it^{1/2}$ *vs* t **Plots of DBDT**
(A) 0.1M TEAB in 75% ethanol; DBDT = 1.0 mM
(B) 0.1M TEAB in 50% isopropanol: DBDT = 0.5mM
(C) 0.05M TEAB in 50% DMF; DBDT = 0.25 mM
(D) 0.02M TBAI in 75% ethanol: DBDT = 0.5mM.

the reduction process is diffusion controlled. The nature of the reverse chronopotentiogram in various supporting electrolytes confirm that the electro reduction is irreversible. Kinetic parameters such as diffusion coefficient, heterogeneous forward rate constants ($k_{f,h}^{\circ}$) and transfer coefficient values of DBDT in different supporting electrolytes are evaluated from different techniques and presented in Table 3.

Table 3

Kinetic Parameters of DBDT in Different Media by Different Techniques

Medium	αn_a		D x 10^5 $cm^2.s^{-1}$			$k^{\circ}_{f,h}$ x 10^6 cm.s^{-1}	
	C.V.	C.P.	C.V.	C.A.	C.P.	C.V.	C.P.
0.1M TEAB in 75% ethanol	0.23	0.26	0.17	0.89	0.63	0.23	0.50
0.1M TEAB in 50% isopropanol	0.19	0.26	0.09	0.36	0.11	0.97	0.72
0.05M TEAB in 50% DMF	0.30	0.30	0.13	0.07	0.10	0.38	0.32
0.02M TBAI in 75% ethanol	0.20	0.32	0.17	1.13	0.93	0.18	0.14

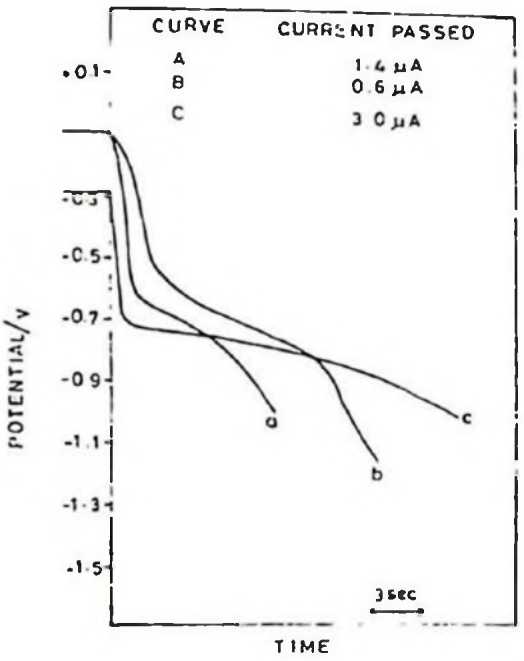


Fig. 3 Typical chronopotentiograms
(A) 0.1M TEAB in 50% inoproponol; DBDT = 0.5mM
(B) 0.05M TEAB in 50% DMF; DBDT= 0.25mM
(C) 0.02M TBAI in 75% ethanol; DBDT= 0.5mM.

Mechanism of the reduction process

The electrochemical reduction process of DBDT is found to be irreversible involving two electron addition. From this data and product analysis, it is suggested that the reduction process of DBDT involves probably two steps, (i) addition of two electrons to DBDT to give $(Br\text{-}C_6H_4\text{-})_2$ CH-CCl_2^- and (ii) simultaneous rapid aquesition of proton from the solvent to give $(Br\text{-}C_6H_4\text{-})_2$ CH-$CHCl_2^-$. This mechanism is quite similar to that of DDT[9]. The change in the nuclear substitution in this compound has no noticeable effect on the reduction of carbon-chlorine bond, which may be due to its distance from benzene nucleus by two carbon atoms.

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