



# **ELECTROCHEMICAL REDUCTIVE DEHALOGENATION OF BROMINATED ORGANIC COMPOUNDS IN WATER-METHANOL MEDIA ON A BORON DOPED DIAMOND ELECTRODE: BULK ELECTROLYSIS**

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## **ABSTRACT**

Electrochemical reduction of 1, 2-dibromoethane, bromoethane and bromobenzene on the Boron-Doped Diamond Electrode (BDDE) was studied in aqueous methanol media. The reaction was carried out at room temperature in the potential region between - 1.5 V and - 2.1 V. The removal of the first bromine from 1, 2-dibromoethane goes smoothly and fast at - 1.5 V; current efficiency is close to 100% in the beginning of the reaction, and even at 90% conversion is almost 60%. The removal of the second (and last) bromine is slower; it takes about 50 hr at - 1.7 V to reach 90% conversion, with current efficiency of about 5%. Bromine can be removed from bromobenzene by electrochemical reduction at potentials more negative than -1.8V. However, even at - 2.1V, the rate constant is small and the estimated current efficiency is less than 1%.

**Key words :** Brominated organic compounds, BDD electrode, Electrochemical reduction.

## **INTRODUCTION**

Recently, electrochemical oxidative destruction of halogenated organic compounds on a Boron-Doped Diamond Electrode became increasingly popular<sup>1,2</sup>. Complete mineralization of halogenated compounds was reported possible at a potential of about 3V, but was considered to be highly energy-consuming<sup>1,2</sup>. Electrochemical reductive dehalogenation - preferably in aqueous solutions - would be a good alternative to oxidation<sup>3-5</sup>. In neutral aqueous solutions, the potential of BDDE can be shifted as far as - 1.8 V vs. the Standard Hydrogen Electrode (SHE) without significant hydrogen evolution<sup>6</sup>. This would be suitable for the reduction of aliphatic, and even some aromatic

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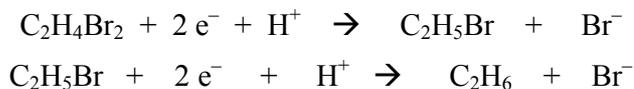
halogen organic compounds<sup>3-5</sup>. The study of electrochemical reduction in pure aqueous media is often associated with problems, such as low solubility and an early start of hydrogen evolution. To avoid such difficulties in this study, we used a 30% vol. aqueous methanol as the solvent, shifting hydrogen evolution to even more negative potentials and increasing solubility, when compared to pure water solutions.

## EXPERIMENTAL

In this work, the reduction of 1, 2-dibromoethane, bromoethane, and bromobenzene was studied at different potentials by constant potential electrolysis on the Boron Doped Diamond Electrode (BDDE) in aqueous methanol media (30 vol.% of MeOH). Polycrystalline thin-film Boron Doped Diamond Electrode (5 micrometer thickness), prepared by hot filament chemical vapour deposition on niobium substrate, was used. Boron content was 3000 ppm, and apparent electrode area was 1.6 cm<sup>2</sup>. The Boron-Doped Diamond Electrode used in this work was provided by Fraunhofer Institut fuer Schicht- und Oberflächentechnik, IST Braunschweig/Germany. As a supporting electrolyte, Na<sub>2</sub>SO<sub>4</sub> (0.04 M) was used. Electrolysis was carried out in a two-compartment glass electrochemical cell with a cathode compartment volume of 22 mL at room temperature. The cathode compartment was constantly stirred by a magnetic stirrer during the course of the reaction. An Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (sat) electrode with a Luggin capillary served as the reference electrode and Pt (1 cm<sup>2</sup>) as counter electrode. The compartments were separated by the cation exchange membrane Nafion-H. The potentiostat used was a computer-controlled Zahner IM6 electrochemical workstation (Zahner-elektric GmbH & Co., Germany). The concentration of bromide ions in solution was measured by a bromide ion selective electrode. All chemicals used were of analytical grade (>99%), except 1, 2-dibromoethane and bromoethane (98%, Aldrich). All solutions were prepared with bi-distilled water. Stock solutions of 1, 2-dibromoethane (0.116 M), bromoethane (0.141 M) and bromobenzene (0.095 M) in methanol were kept in the dark, and aliquots of these solutions were used to prepare working solutions of different concentrations.

## RESULTS AND DISCUSSION

1, 2-dibromoethane concentration decreases exponentially at - 1.5 V (Fig. 1). Current also decreases during electrolysis (Fig. 1), but at a smaller rate, showing decrease of current efficiency at smaller concentrations of 1, 2-dibromoethane. Concentrations of 1, 2-dibromoethane presented in Fig. 1 were calculated through bromide ion measured concentrations and a material balance equation. However, in the case of polyhalogenated substances the reaction goes stepwise<sup>3</sup>:



This could give some error, if the second bromine removal proceeds easily enough compared to the first bromine removal. To check this, electrolysis of bromoethane was carried out at the same potential - 1.5 V, and results were compared to 1, 2-dibromoethane debromination. Both reactions can be described by the apparent first order rate equation (Eq. 1).

$$-d[\text{Reactant}]/dt = k[\text{Reactant}] \quad \dots(1)$$

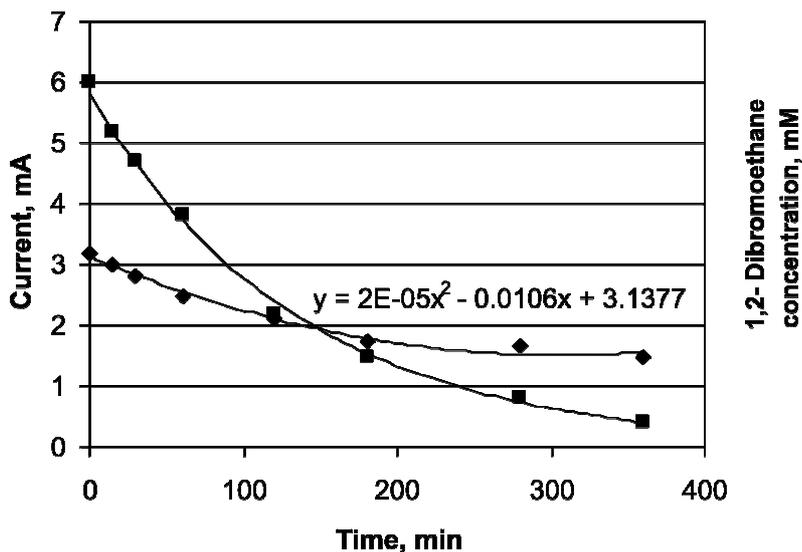
Presented in logarithmic form, this equation allows for the calculation of the apparent first order rate constant from the slope of the corresponding graph (Fig. 2). Data in Fig. 2 show that the rate constant of bromoethane debromination is approximately 30 times smaller as compared to 1, 2-dibromoethane debromination. Using the theory of consecutive first order reactions<sup>7</sup> and rate constants presented in Fig. 2, we calculated concentration profiles of 1, 2-dibromoethane (reactant), bromoethane (intermediate) and ethane (final product) for an initial concentration of 1, 2-dibromoethane equal to  $6 \times 10^{-3}$  M. Data presented in Fig. 3 confirms that removal of the second bromine does not influence the kinetics of the first bromine removal until 90% conversion of 1, 2-dibromoethane, and even after this, the influence is negligibly small. Current efficiency for the removal of the first bromine from 1, 2-dibromoethane is close to 100% at the beginning of the reaction, and even at 90% conversion is almost 60% (Table 1).

**Table 1. Efficiency of electrochemical reductive removal of the first bromine from 1, 2-dibromoethane.  $[\text{C}_2\text{H}_4\text{Br}_2]_0 = 6 \times 10^{-3}$  M, volume 22 mL. In calculations, the rate constant presented in Fig. 2 and the integrated equation for the current curve presented in Fig. 1 were used.**

Conversion/%	10	25	50	75	90
Time/min	14.3	39.0	93.6	188	312
Quantity of electricity necessary/Q	2.55	6.38	12.8	19.1	23
Quantity of electricity spent/Q	2.61	6.85	15.1	26.8	39.8
Current efficiency/%	98	93	85	71	58

Considering the data presented in Fig. 1, Fig. 2 and in Table 1, we can conclude

that reductive electrochemical removal of all but the last bromine from polybrominated aliphatic compounds can be done easily, with high current efficiency (the larger is the number of halogen atoms, the easier is the removal<sup>3</sup>). Reduction of bromoethane with removal of the last bromine requires more negative potentials (Fig. 2, Fig. 4), and even at a potential of - 1.7 V the rate of reaction is 10 times smaller than that reached for 1, 2-dibromoethane at - 1.5 V. The removal of the last bromine from bromoethane is possible, but it requires about 50 estimated hours to reach 90% conversion, with a current efficiency of about 5%. Most difficult is the electrochemical reductive dehalogenation of aromatic halogenorganic compounds<sup>3, 4</sup>. Chlorinated aromatic compounds cannot be completely dechlorinated in aqueous solutions, and even in non-aqueous solvents, like DMSO and acetonitrile, removal of the last chlorine is difficult<sup>4</sup>. According to data<sup>3</sup>, bromoaromatic compounds can be removed more easily as compared to chloroaromatic ones. Data in Fig. 5 shows that the last bromine can be removed from bromobenzene by the electrochemical reduction on the BDDE in 30% methanol at potentials between - 1.8 V and - 2.1 V. However, the rate constant even at - 2.1 V is much smaller than for bromoethane, and estimated current efficiency is less than 1%. At potentials more negative than - 2.1V BDDE deteriorates after 10 hours of work.



**Fig.1. Current and conversion of 1, 2-dibromoethane vs. electrolysis time.**

$E = - 1.5 \text{ V vs. SHE}$ ,  $[C_2H_4Br_2]_0 = 6 \times 10^{-3} \text{ M}$ . Equation on the graph describes Current vs. Time.

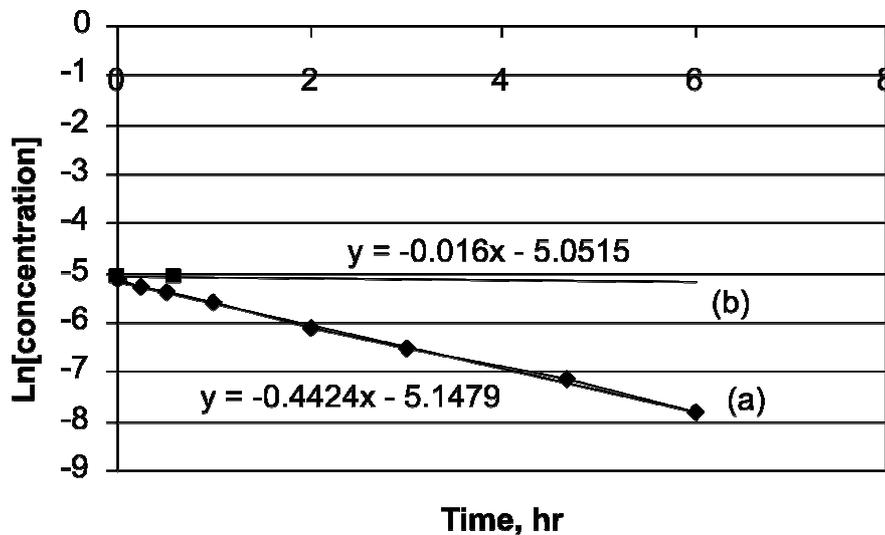


Fig. 2 : Kinetics of electrochemical reduction of  $C_2H_4Br_2$  (a) and  $C_2H_5Br$  (b) at -1.5 V. Rate constants are  $0.44\text{ hr}^{-1}$  and  $0.016\text{ hr}^{-1}$ .

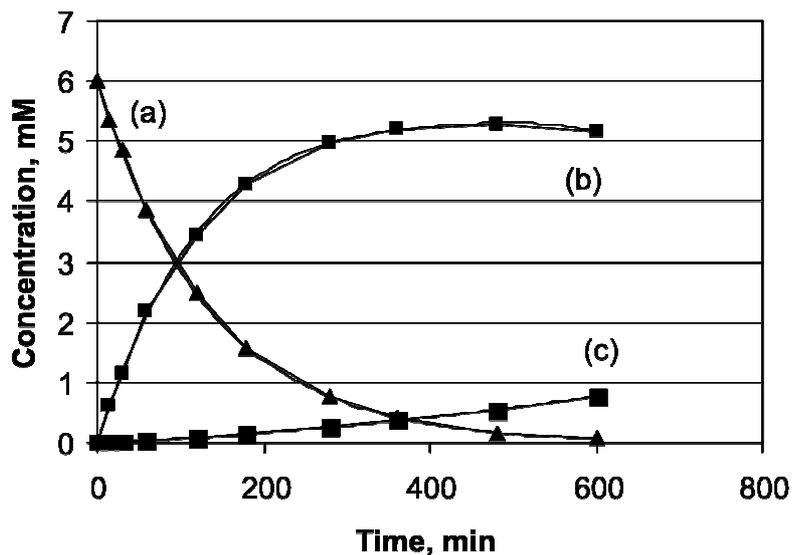


Fig. 3. Concentrations vs. time calculated with use of consecutive reactions theory and rates constants from Fig. 2(a)  $C_2H_4Br_2$ , (b)  $C_2H_5Br$ , (c)  $C_2H_6$ .

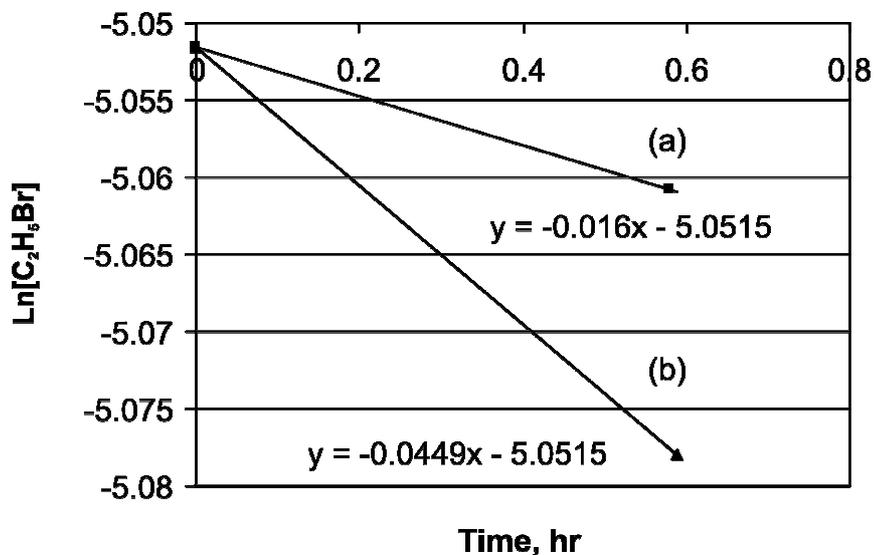


Fig. 4. Influence of potential on the rate of reduction of  $C_2H_5Br$ . (a)  $-1.5\text{ V}$ , (b)  $-1.7\text{ V}$ .

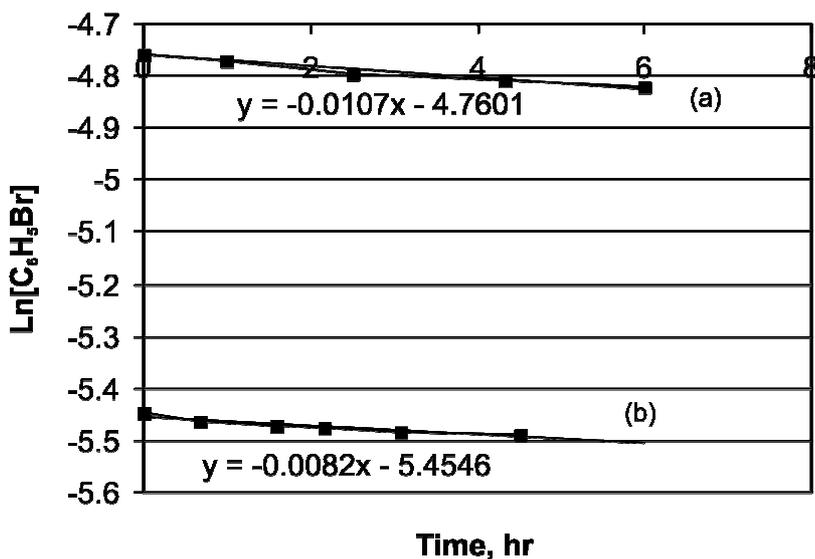


Fig. 5. Kinetics of electrochemical reductive debromination of  $C_6H_5Br$ . (a)  $[C_6H_5Br]_0 = 8.6\text{ mM}$ ,  $E = -2.1\text{ V}$ , (b)  $[C_6H_5Br]_0 = 4.3\text{ mM}$ ,  $E = -1.8\text{ V}$ .

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