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Electrochemical reactions of halohydrins.
I. Attempt at reductive coupling

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The electrochemical reductive coupling of 2-chloroethanol and 2-bromoethanol to 1,4-butanediol was attempted. The electrochemical cleavage of the carbon–halogen bond leads to intermediates which are either unstable and decompose to ethylene and OH^-, or undergo chemical reactions leading to ether formation. The presence of the hydroxyl group in halohydrins seems to be responsible for the observed reaction paths. When the alcohol group was protected by esterification, coupled products were observed. Coupling of bromoethyl acetate to 1,4-butanediol diacetate thus appears technically feasible, but is a commercially less attractive route to 1,4-butanediol.

1. Introduction

The objective of the present work has been to determine the feasibility of the electrochemical reductive coupling of halohydrins to 1,4-butanediol. 1,4-Butanediol is used in the production of poly(butylene terephthalate), a material which has substantial potential for market growth. The present method of producing 1,4-butanediol is based on acetylene and formaldehyde raw materials. The reaction visualized would proceed as follows

$$2ClCH_2CH_2OH + 2e \rightarrow HO(CH_2)_4OH + 2Cl^-.$$

Examination of the literature suggests that this particular reaction has not been studied electrochemically. Coupled products are, however, observed in certain electrochemical reductions of organic halides, such as ethyl and butyl iodide, 3-iodopropionitrile, and *p*-nitrobenzyl bromide.

The chemical reduction of 2-chloroethanol to 1,4-butanediol by metallic copper was patented in 1946 [1]. The reaction was supposedly carried out for 48 hours at 125–175° C. No yields of 1,4-butanediol were given. More recently the coupling of 2-bromoethanol to 1,4-butanediol was claimed in one of a series of patents [2–4] dealing with the coupling of some substituted alkyl halides by active metals or metallic salts. No actual experiments were described.

Apart from 2-chloroethanol, 2-bromoethanol and 2-iodoethanol were studied to various degrees in the course of this work.

2. Experimental

2.1. *Potentiodynamic measurements*

The cell used for the potentiodynamic studies was of a conventional type with anolyte and catholyte separated by a fritted glass disc. A calomel reference electrode was used to monitor electrode potentials of the working electrode. The electrical equipment used in potentiodynamic measurements consisted of a Function Generator, Model CHF-1 Elscint, a Wenking Potentiostat and a Hewlett-Packard Autograph Model 7030AM *X–Y* Recorder.

2.2. *Constant current electrolysis*

Synthetic work was carried out by electrolysis at constant current (Hewlett-Packard, 6264B d.c. power supply). The amount of charge passed was monitored by a current integrator (Model 1002, Curtis Instrument, Inc.). The electrolysis cell used for preparative studies was of a plane parallel configuration with the anode and cathode separated by either the cation or anion exchange membrane. In some cases, a one-compartment cell was

Table 1. Electrolytic conditions for constant current electrolysis

Cell feature	*Composition or value*
Cathode	Pb or Cu. Also: Au, Ag or Ni. ($80\ \mathrm{cm}^2$ geometric area)
Anode	Pt/Ta or Ni
Cell	with/without diaphragm
Diaphragm	Cation or anion exchange membrane (Ionics 61 DYG 067 or AMF-A 100)
Solvent	none, DMF
Electrolyte	R_4NX, LiX X = halides or *p*-toluenesulphonate
Anolyte	H_2SO_4
Current density	$10\ \mathrm{mA\ cm}^{-2}$
Temperature	generally 18° C (down to −20° C in some cases)

employed. Cell temperature was maintained by circulating the anolyte (25% aqueous sulphuric acid) or by dipping the cell into the cooling bath (one-compartment cell). Various electrode materials were tested as cathodes, while the anode usually was platinum-clad tantalum and occasionally nickel. Gas evolved at the cathode was collected and analysed by mass spectroscopy (AEI ms 902 Mass Spectrometer, ionizing voltage 70 eV) and GC (25–240° C/30° C/min on 5 ft Carbosieve B). The concentration of catholyte was monitored by GC (100–240° C/10°/min, 8 ft × 1/4 in Porapak P; *n*-butanol internal standard) and product determined by GC–mass spectroscopy (75–250° C/10°/min, 5 ft 5% Carbowax on Diatoport S). A Finnigan Model 3300 gas chromatograph/mass spectrometer operated in the chemical ionization mode was used in this work. The identity of major products was confirmed by comparison with authentic samples. The electrolytic conditions for the constant current electrolysis are summarized in Table 1. In a typical run, charges of 0·3–0·5 Faradays were passed.

3. Results and discussion

3.1. *General*

The electrochemical reduction of various organic halides has been studied extensively [5–11]. Most of the studies employed polarographic rather than steady-state techniques. A few attempts were made to isolate and/or analyse products obtained from the cleavage of carbon–halogen bonds. Elucidation of the mechanism of reduction is thus based mainly on polarographic data obtained in aqueous systems (mercury electrode).

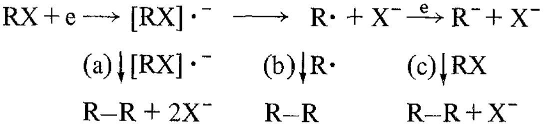
Coupled products are observed in a number of electrochemical reductions of organic halides [7] but seldom with non-activated halides. The possible routes to dimers are [8]:

(a) Interaction of two anion radicals of a parent halide;

(b) Radical recombination;

(c) Nucleophilic attack of R^- upon a parent molecule.

The following scheme will illustrate these options



$$\begin{array}{ccc}\mathrm{RX}+e\longrightarrow[\mathrm{RX}]^{\cdot -} & \longrightarrow\ \mathrm{R}\cdot+\mathrm{X}^- & \xrightarrow{e}\mathrm{R}^-+\mathrm{X}^- \\ (a)\downarrow[\mathrm{RX}]^{\cdot -} & (b)\downarrow\mathrm{R}\cdot & (c)\downarrow\mathrm{RX} \\ \mathrm{R{-}R}+2\mathrm{X}^- & \mathrm{R{-}R} & \mathrm{R{-}R}+\mathrm{X}^-\end{array}$$

According to Baizer the bulk of the experimental evidence supports the radical recombination mechanism, and/or R^- attack on a parent molecule [8].

3.2. *Potentiodynamic measurements*

3.2.1 Current–potential profile of electrode reactions. Potentiodynamic measurements were carried out with lead or copper electrodes in tetraethylammonium *p*-toluenesulphonate/DMF electrolytes with small additons of water. A typical concentration would be 1×10^{-2} M of depolarizer in $R_4N^+/H_2O/DMF = 25/5/70$ wt%. Where indicated, silver and gold electrodes were used. Nickel, cobalt and aluminum electrodes were also tested.

By recording current–potential curves on either electrode in supporting electrolyte system, no current increase was observed prior to hydrogen evolution. A small adsorption peak was observed in some cases. Addition of 2-chloroethanol did not alter the basic *i–E* curve when Pb or Cu were used as cathodes. Introduction of 2-bromoethanol changed the *i–E* profile indicating reduction of 2-bromoethanol at potentials much lower than those needed for hydrogen evolution. Gas evolution was observed at the electrode surface. The reduction of 2-iodoethanol required potentials still lower than 2-bromoethanol. It was also accompanied by gas evolution, These reactions are illustrated in Fig. 1.

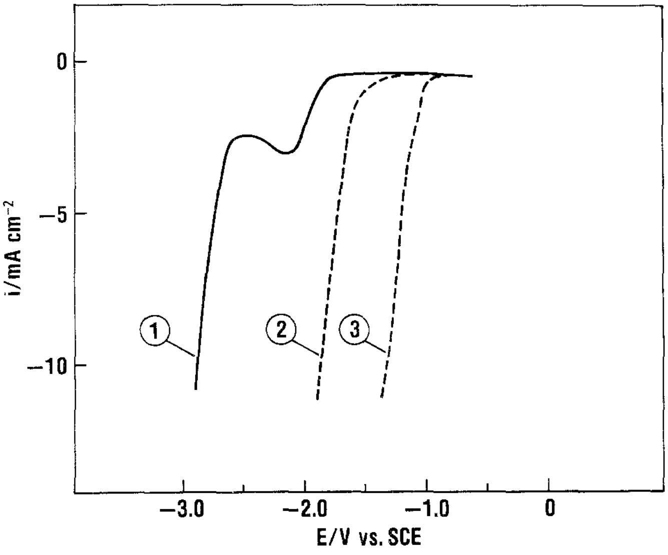


Fig. 1. The current–potential profiles of electrode reactions on lead in tetraethylammonium p-toluenesulphonate/H_2O/DMF supporting electrolyte (25/5/70 wt%): Pure electrolyte and upon addition of 10^{-2} M 2-chloroethanol (1), 10^{-2} M 2-bromoethanol (2), and 10^{-2} M 2-iodoethanol (3). Sweep rate 50 mV s^{-1}, temperature 25° C.

The reduction of 2-chloroethanol was observed at high negative potentials only on silver and gold. This indicates that adsorption [12], prior to the reduction, may play an important role in halide reduction. The absence of 2-bromoethanol reduction on aluminum supports this finding. A summary of potential sweep data is given in Table 2. The reduction potentials listed correspond to the rate of 10 mA cm^{-2}.

3.2.2. Effect of Cu$^+$ addition on 2-bromoethanol and 2-iodoethanol reductions. The electrochemical reduction of 2-bromoethanol takes place at high negative potentials (− 1·9 V versus SCE at 10 mA cm^{-2}) and is seen as one two-electron step. This suggests that the transfer of the first electron is the rate-determining step. It is followed by rapid transfer of the second electron leading to an anionic species. Thus, since the first electron is added to the organic molecule at very negative potentials and since it is known that radical anions and radical species are easier to reduce than neutral molecules, the formed intermediates have little chance of undergoing any other reaction, e.g. coupling but further reduction. Therefore, no coupling via radical or radical anion mechanisms could be expected under these conditions. The same behaviour was observed in 3-bromopropionitrile reduction, in which case no coupled products were obtained [10].

The formation of coupled products was observed in the reduction of 3-iodopropionitrile. 3-Iodopropionitrile is reduced at substantially lower potential than 3-bromopropionitrile and it was seen polarographically as two one-electron steps [10]. The half-wave potentials were highly dependent on 3-iodopropionitrile concentration ($\Delta E_{1/2}$ higher at higher reactant concentrations).

It was anticipated, therefore, that by lowering the potential required for reduction of 2-bromoethanol (and 2-iodoethanol) the chance for formation of coupled products would be increased. Recently it was reported that monolayers of some metals deposited on electrodes catalysed several reactions [13]. For example, the rates for anodic oxidation of formic acid were about two orders of magnitude higher on a platinum electrode covered with monolayers of Pb^{2+}, Bi^{3+}, and Tl^+ than on bare platinum [13–15]. No similar results were reported for cathodic organic reactions. We have studied the effect of the addition of small amounts (10^{-2} M to 10^{-3} M) of various salts (Pb^{2+}, Fe^{2+}, Ni^{2+}, Tl^+, Ag^+, Cu^+) on the electrochemical reduction of 2-bromoethanol and 2-iodoethanol. A substantial shift in the reduction potential of 2-bromoethanol on lead towards more positive values was observed with additions of Cu^+ and Ag^+. No change in reduction potential of 2-iodoethanol was noticed. The reduction of 2-bromoethanol remained a one step process and was accompanied by gas evolution. Interestingly enough, however, a similar effect was observed with a copper cathode upon addition of Cu^+. This suggests that some other mechanism(s),

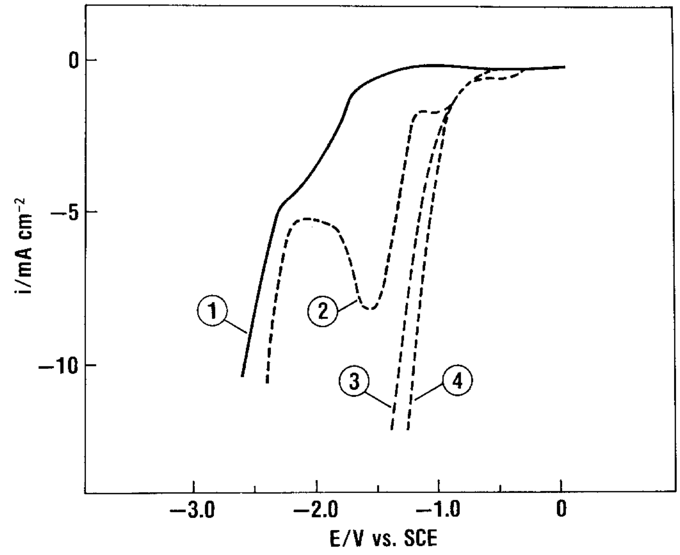


Fig. 2. Effect of Cu$^+$ addition on 2-bromoethanol reduction on copper electrode: $Bu_4N^+/H_2O/DMF$ (25/5/70 wt%) supporting electrolyte (1), 10^{-3} M Cu$^+$ (2), 10^{-3} M Cu$^+$ + 10^{-2} 2-iodoethanol (3), 10^{-3} M Cu$^+$ + 10^{-2} 2-bromoethanol (4). Sweep rate 50 mV s^{-1}, temperature 25° C.

rather than catalysis by foreign metal monolayers, may be responsible for the observed phenomena. This aspect deserves further attention. The effect of Cu$^+$ addition on 2-bromoethanol reduction is illustrated in Fig. 2 and Table 2. Other metals studied had little or no effect.

3.3. *Constant current electrolysis*

3.3.1. 2-Chloroethanol. The constant current electrolysis on either Pb or Cu was ineffective. Hydrogen was the main product. With gold-plated lead, a high content of ethylene was found in the collected gas. The ethylene:hydrogen ratio was 4:1 as determined by mass spectroscopy. The total gas volume corresponded to 100% current efficiency. The electrolysis was carried out in a two-compartment cell (cation exchange separator) in DMF. When neat 2-chloroethanol was electrolysed in a one-compartment cell, using Ni electrodes, only 40% of the charge passed went to gas evolution. The ethylene:hydrogen ratio was 1:6. Analysis of the solution indicated that $Cl(CH_2)_2O(CH_2)_2OH$ was the main product.

3.3.2. 2-Bromoethanol. The constant current electrolysis of 2-bromoethanol on Cu or Pb in DMF (two-compartment cell, cation exchange

Table 2. Potential sweep data for halohydrin reductions[*]

	E_{10} (mV versus SCE)				
Reactant	*Pb*	*Cu*	*Au*	*Ag*	*Al*
$ClCH_2CH_2OH$	NR[†]	NR			
$ClCH_2CH_2OOCCH_3$	NR	NR	−2·5	−2·3	
$BrCH_2CH_2OH$	−1·9	−1·9			NR
	−1·4[‡]	−1·1[§]	−1·4[‖]		
	−1·6[‖]				
$BrCH_2CH_2OOCCH_3$	−1·8	−1·8			
	−1·3[‡]				
ICH_2CH_2OH	−1·3	−1·3	−1·3		
$HOCH_2CH_2OOCCH_3$	NR	NR	NR		

[*] Sweep rate, 50 mV s^{-1}; temperature, 25° C.
[†] NR = no reaction. [‡] 10^{-2} M Cu$^+$ present.
[§] 10^{-3} M Cu$^+$ present. [‖] 10^{-3} M Ag$^+$ present.

*Table 3. Constant current electrolysis of bromoethanol**

Electrode and cell	*Electrolyte*	*Products*	*Current efficiency (%)*
Cu or Pb, cation exchange membrane	DMF/TEAS† or TBAB‡	C_2H_4/H_2 (11:1)	100 w/wo Cu^+
Cu, cation exchange membrane	$CH_2{=}CH{-}CN$§ TEAS†	C_2H_4/H_2 (15:1)	50
		$HO(CH_2)_4CN$	20
	DMF/TEAS†	C_2H_4/H_2 (100:1)	–
	1, 3-butadiene	no coupling with 1,3-butadiene	
Cu, anion exchange membrane	DMF/LiBr//	C_2H_4/H_2 (200:1)	40
		$Br(CH_2)_2{-}O{-}(CH_2)_2OH$	–
		$Br(CH_2)_2{-}O{-}CH{=}CH_2$	–
		other	–

* Substrate/R_4N^+/solvent = 50/25/25 wt%.
† Tetraethylammonium *p*-toluenesulphonate.
‡ Tetrabutylammonium bromide.
§ 0·1 wt% hydroquinone present.
// Substrate/DMF/LiBr = 60/35/5 wt%.

separator) was accompanied by gas evolution corresponding to 100% current efficiency. The collected gas was an ethylene/hydrogen mixture in an 11:1 ratio. The addition of 10^{-3} M CuBr had no apparent effect. The electrolysis runs were carried out in the temperature range of −20 to 20° C and with current densities of 10 and 100 mA cm^{-2}. No effect of temperature or current density on the reaction products and current efficiency was observed.

When DMF solvent was replaced by acrylonitrile, gas evolution proceeded with 50% current efficiency. Analysis by GC and mass spectrometry indicated that a number of different products were present, with $HO(CH_2)_4CN$ being the main product (Table 3). No coupling products of 2-bromoethanol with butadiene could be detected when butadiene was bubbled through the electrolyte during the electrolysis (DMF as a solvent).

The electrochemical reduction of 2-bromoethanol under the same condition (DMF solvent) but with an anion exchange membrane separating cathodic and anodic compartments gave results similar to those obtained with 2-chloroethanol in a one-compartment cell. Gas evolution was decreased to 40% current efficiency but the ethylene:hydrogen ratio was 200:1. In the liquid phase, $Br(CH_2)_2{-}O{-}(CH_2)_2OH$ was detected among the products. Both reactions had one common feature: the water content was below 1%, as compared to 1–5% when cation exchange separators were used*.

3.3.3. 2-Iodoethanol. Reduction of 2-iodoethanol on Pb in DMF proceeded with extensive disintegration of the lead cathode and formation of an organo-lead compound; the elemental analysis of this corresponded to $C_8H_{23}PbI_3$. No hydroxyl band could be detected by i.r.

Although formation of an organo-lead compound may suggest alkyl radical formation in the reduction of 2-iodoethanol, no coupled products could be detected when Cu was used instead of Pb as the cathode. With acrylonitrile and CuBr as electrolyte, gas evolution corresponded to 50–75% of the charge passed. In the liquid phase, $BrCH{=}CH_2$ and $ICH{=}CH_2$ were detected among the products. The same results were obtained

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* In all two-compartment cells aqueous anolyte was used. Thus, along with H^+, water was transferred to the cathodic compartment. With anion exchange membranes water transfer was prevented. Anion exchange membranes, however, decomposed rapidly under the conditions employed.

regardless of whether cation or anion exchange membranes were used.

3.3.4. 2-Bromoethyl acetate. The reduction of 2-bromoethyl acetate was studied along with 2-bromoethanol in order to determine the influence of substituents on the C—Br cleavage potential. Potential sweep measurements showed that the presence of ester groups shifted the reduction potentials by 100 mV in the positive direction. Constant current electrolysis in DMF produced ethylene and hydrogen (14:1) with 100% current efficiency when 1–5% water was present (cation exchange separator). Substituting LiBr for R_4NBr decreased the gas evolution somewhat. There is no obvious explanation. When the electrolysis was carried out in a system where the H_2O content was reduced to below 1% (anion exchange separator), the coupling of bromoethyl acetate was achieved. The current efficiency for $AcO(CH_2)_4OAc$ formation was estimated to be 30% (based on GC analysis) at low conversions. Due to the difficulties experienced with anion exchange membranes, the electrolysis was not run long enough to assess yields at high conversion. The gas evolution proceeded with 40% current efficiency. The ethylene:H_2 ratio was 10:1.

The electrolysis of neat bromoethyl acetate in a one-compartment cell also gave a coupled product although at somewhat lower yield. A number of other unidentified products were also detected (Table 4).

3.4. *Speculative mechanisms*

Based on experimental evidence, one can conclude that no single mechanism can explain the reduction paths of various halohydrins. The picture is complicated even further by the high sensitivity of the reduction mechanism to the electrolytic conditions employed. It has been shown that the water content of the electrolyte plays an essential role as reflected by the change in the type of products.

In the present work no attempt was made to study reaction mechanisms other than by examination of the type of products formed. The mechanistic conclusions are, therefore, tentative and only generalized schemes can be suggested. These are as follows

*Table 4. Constant current electrolysis of bromoethyl acetate**

Electrode and cell	*Electrolyte*	*Products*	*Current efficiency (%)*
Cu or Pb, cation exchange membrane	DMF, TEAS† or TBAB‡	C_2H_4/H_2 (14:1)	100
	DMF/LiBr§	C_2H_4/H_2	90
Cu, anion exchange membrane	DMF/LiBr§	C_2H_4/H_2 (10:1)	40
		$AcO(CH_2)_4OAc$	30
		$BrCH{=}CH_2$	–
		other	–
Ni, one-compartment cell	LiBr	C_2H_4/H_2	40
		$AcO(CH_2)_4OAc$	20
		$BrCH{=}CH_2$	–
		other	–

* Substrate/R_4N^+/DMF = 50/25/25 wt%.
† Tetraethylammonium *p*-toluenesulphonate.
‡ Tetrabuthylammonium bromide.
§ Substrate/LiBr/DMF = 60/35/5 wt%.

(a) Chloroethanol

One electron:

$$\begin{tikzcd}[column sep=small]
\mathrm{ClCH_2CH_2OH} \arrow[r, "e"] & \mathrm{H} \arrow[d, "\mathrm{H}"'] & + & \mathrm{ClCH_2CH_2O^-} \arrow[d, "\mathrm{ClCH_2CH_2OH}"] \\
& \mathrm{H_2} & & \mathrm{ClCH_2CH_2OCH_2CH_2OH + Cl^-}
\end{tikzcd}$$

Two electron:

$$\mathrm{ClCH_2CH_2OH} \xrightarrow{2e} \mathrm{Cl^- + {}^-CH_2CH_2OH} \longrightarrow \mathrm{C_2H_4 + OH^-}$$

(b) Bromoethanol
Two electron:

$$\begin{tikzcd}[column sep=small]
\mathrm{BrCH_2CH_2OH} \arrow[r, "2e"] & \mathrm{Br^- + {}^-CH_2CH_2OH} \arrow[r] \arrow[d, "+\ \mathrm{BrCH_2CH_2OH}"] & \mathrm{C_2H_4 + OH^-} \\
& \mathrm{BrCH_2CH_2O^- + CH_3CH_2OH} \arrow[d, "\mathrm{Br\ CH_2CH_2OH}"] & \\
& \mathrm{BrCH_2CH_2OCH_2CH_2OH + Br^-} &
\end{tikzcd}$$

(c) Bromoethyl acetate
One electron:

$$\begin{tikzcd}[column sep=small]
\mathrm{BrCH_2CH_2OAc} \arrow[r, "e"] & \mathrm{\cdot CH_2CH_2OAc + Br^-} \arrow[d, "\mathrm{\cdot CH_2CH_2OAc}"] \\
& \mathrm{AcO(CH_2)_4OAc}
\end{tikzcd}$$

2-Iodoethanol is excluded from these speculations because of the limited data collected.

4. Summary

The studies of halohydrins reduction were carried out under a variety of electrolytic conditions. The results can be summarized as follows:

(a) The products of halohydrin reduction depend greatly on the availability of water in the system and on the nature of the starting compound.

(b) At higher water concentrations (H_2O content 1–5%) reduction of chloroethanol and bromoethanol proceed via one two-electron step, leading to ethylene as a main product (90% current efficiency). The postulated carbanion intermediate was successfully trapped with acrylonitrile.

(c) At low water concentration (H_2O content below 1%), both chloroethanol and bromoethanol form ethers. The second major product is hydrogen in the case of chloroethanol, and ethylene when bromoethanol is the reactant.

(d) Coupling is observed only with halohydrin esters, namely bromoethyl acetate, at low proton concentrations (20–30% current efficiency). A radical mechanism is postulated in this case.

Acknowledgements

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