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Electrochemical reactions of halohydrins. II. Olefins formation

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2-Bromoethanol was reduced to ethylene, 1-bromo-2-propanol to propylene, and 2-bromo-1-indanol to indene on Pb or Cu electrodes with R_4N^+ electrolytes, in DMF with and without addition of water. Material and current efficiencies were high. Hydrogen was the only by-product in all cases. It is suggested that this represents a general method for the conversion of bromohydrins to olefins.

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1. Introduction

The reduction of various bromohydrins to olefins with low-valent titanium (4 molar equivalent $LiAlH_4$ to 1 molar equivalent $TiCl_3$ in THF) was reported recently [1]. The scarcity of direct methods devised to effect this reaction which is claimed to be of some importance in synthesis was pointed out in the same publication. We wish to report, therefore, the electrochemical eliminative reduction of bromohydrins to olefins. Our work suggests that electrochemistry might provide a convenient method for effecting such reactions under a variety of conditions.

2. Experimental

The work was carried out by electrolysis at constant current using the equipment and cell described in the preceding paper [2]. Anodic and cathodic compartments were separated by a cation exchange membrane (Ionics 61 DYG067). Other separators were not tried, although an inert porous material might have been suitable. All chemicals (commercially available) were used without further purification or drying. Most of the experiments were performed at a current density of $10\,mA\,cm^{-2}$. A higher current density ($100\,mA\,cm^{-2}$) led to the same product. In a typical run, charges of 0·3–0·5 Faradays were passed. The gas evolved at the cathode was collected, and its volume determined. The product identification of gas and liquid samples and analyses were performed by GC, mass spectrometry and GC–mass spectrometry [2]. Comparison of retention times with authentic samples was done where necessary.

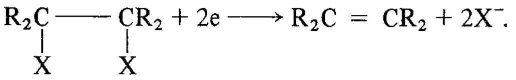
3. Results and discussion

The electrochemical reduction of monosubstituted alkyl halides in protic media generally leads to the formation of the corresponding saturated hydrocarbons, according to the following overall equation [3]

$$RX + 2e + 2H^+ \longrightarrow RH + HX$$

where X = Cl, Br, I.

Instances of double bond formation are reported in the cases of some α, β-dihalides [3, 4]. The reaction proceeds apparently in a concerted fashion without the participation of protons in the rate-determining step [4]



$$\underset{X}{\underset{|}{R_2C}} - \underset{X}{\underset{|}{CR_2}} + 2e \longrightarrow R_2C = CR_2 + 2X^-.$$

Data on the electrochemical reduction of halohydrins are sparse. No data could be found relating to bromohydrin reduction. The formation of ethylene from 2-iodoethanol in high yields (85%) was reported [5]. The work was carried out in aqueous solution on a mercury electrode. This appears to be the only known example of the electrochemical eliminative reduction of simple

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Table 1. Constant current electrolysis of halohydrins[a]

Substrate	*Electrode*	*Product*[b]	*Current efficiency (%)*
2-Chloroethanol[c]	Au (on Pb)[d]	ethylene	ND[e]
2-Chloroethyl acetate[f]	Au (on Pb)[d]	ethylene	80
2-Bromoethanol[f]	Pb or Cu	ethylene	95
2-Bromoethyl acetate[f]	Pb or Cu	ethylene	95
2-Iodoethanol[g]	Cu	ethylene	85
1-Bromo-2-propanol[h]	Pb	propylene	70
	Cu	propylene	45
1, 3-Dibromo-2-propanol	Cu	propylene	ND
2-Bromo-1-indanol	Pb[h]	indene	85–100
	Cu[i]	indene	67

[a] current density = 10 mA cm^{-2}, temperature = 18–20° C.
[b] Hydrogen is the sole by-product.
[c] See [2].
[d] Reduction of chloro-derivatives does not take place on Pb or Cu.
[e] ND = not determined.
[f] Substrate/R_4N^+/DMF = 50/25/25 wt%.
[g] Substrate/R_4N^+/sulpholane = 20/30/50 wt%.
[h] Substrate/R_4N^+/DMF = 30/25/45 wt%.
[i] Substrate/R_4N^+/DMF/H_2O = 20/30/46/4 wt%.

halohydrins to olefins. Olefin formation via cleavage of halogen and oxygen bonds was, however, observed in controlled potential electrolysis of some complex 2-haloethoxy esters [6]. Bond activation through substituent effects should be expected in these cases.

During the course of our study of the electrochemical reduction of simple halohydrins on solid electrodes in organic or aqueous organic electrolytes [2], it was found that 2-bromoethanol produced ethylene with 95% current and 100% material yields. 2-Chloroethanol (gold cathode) and 2-iodoethanol behave in much the same way. In all these cases, olefins were formed with up to 100% current efficiency. No other products except hydrogen could generally be detected. An exception was the reduction of 2-iodoethanol on a lead electrode. Severe disintegration of the lead cathode was observed, with the formation of organo-lead compound(s) of undetermined structure [2].

In order to assess the possible general applicability of the electrochemical method for olefin formation from halohydrins (bromohydrins in particular), the work was extended to several other compounds (Table 1). A series of constant current electrolyses of bromohydrins was carried out on copper and lead cathodes in DMF solvent, with and without addition of water. In accordance with our expectation, propylene was detected as the only product of 1-bromo-2-propanol reduction on both copper and lead. The total volume of gas collected (propylene + hydrogen) corresponded to 100% current efficiency*, based on a two-electron process. The propylene content of the collected gas was lower with a copper cathode under otherwise identical conditions. The propylene content gradually decreases with time on both copper and lead indicating that the process efficiency depends on the water content in the catholyte. The latter increases with time, due to transfer from the anodic compartment. The lower current efficiency observed with a copper electrode is thus due to the preferential hydrogen evolution on this electrode.

In the case of 1, 3-dibromo-2-propanol, propylene rather than bromopropylene (or bromopro-

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* Hydrogen evolution obviously represents process inefficiency.

pane) was the main product observed. Further reduction of the substrate (or preferential reduction of the substituent) is thus to be expected in substituted halohydrins containing reducible substituents.

Reduction of 2-bromo-1-indanol produced indene as the only product in all investigated cases. On lead, the gas collected at the cathode totalled 0 ml after 0·02 F, 20 ml after 0·04 F and 345 ml after 0·2 F passed. The collected gas was hydrogen. This amounts to 0%, 5% and 15% current efficiency for hydrogen evolution of 100%, 95% and 85% for bromohydrin reduction, respectively. The increase in hydrogen evolution is clearly related to an increase in water content in the cathode chamber with time, due to its transfer from the anodic compartment. The reduction of 2-bromo-1-indanol on copper was conducted with water added to the starting catholyte. Even so, indene was formed with a high current efficiency (67% after 0·22 F passed). The electrode material apparently has no influence on the reduction of bromohydrins other than affecting its current efficiency through the competing hydrogen evolution (high versus medium hydrogen overpotential for lead and copper cathodes, respectively). The substantial effect of electrode material was seen only in the case of chloro-derivatives and then only when extended to other metals (2-chloroethanol and 2-chloroethyl acetate are not reduced on copper and lead).

The reduction of halohydrins to olefins proceeds with an overall transfer of two electrons per molecule. The reaction mechanism was not elucidated in detail, however.

It is worth pointing out that 2-bromoethyl acetate (on Pb and Cu) and 2-chloroethyl acetate (on gold-plated lead) also produce ethylene whenever water was present in the catholyte. This work is described elsewhere [2].

4. Summary

Olefins can be formed by electroreduction of halohydrins with up to 100% current efficiency and up to 100% material yield, depending on the electrolytic conditions and the starting material. The presence of water (in DMF) has adverse effects on the process efficiency, although fairly efficient reductions can be conducted with up to 5% water present. Lead appears to be the more efficient cathode material due to its high overpotential for hydrogen evolution. The reaction proceeds with an overall transfer of two electrons. Substituted halohydrins with a reducible substituent(s) may undergo further reduction. The synthetic value of the electrochemical method for effecting olefins formation from halohydrins (preferably bromohydrins) should be considered where appropriate.

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