## ELECTROCHEMICAL CHLORINATION OF BUTADIENE

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An Electrochemical chlorination of butadiene was investigated at 25 °C by using an H-type cell with a CoCl<sub>2</sub>-MeCN anolyte and an  $NH_{4}Cl-H_{2}O$  catholyte separated by an anion-exchange membrane. The electrolysis gave 3,4-dichloro-1-butene and trans-1,4-dichloro-2butene in high current efficiencies.

3,4-Dichloro-l-butene (3,4-DCB) and trans-l,4-dichloro-2-butene (trans-l,4-DCB) are important industrial materials for the synthesis of chloropurene, which is usually produced from butadiene and chlorine by chemical reaction at about 300 °C. To our knowledge, the paper of Tomilov et al.<sup>1)</sup> is the first and the only one dealing with the electrochemical chlorination of butadiene. However, they obtained neither 3,4-DCB nor trans-1,4-DCB. We report in this paper a successful method of electrochemical preparation of these substances in high current efficiencies.

Potentiostatic electrolyses were performed by use of a pyrex-glass H-type cell with a separator of a glass frit or an Asahi Glass ASV anion-exchange membrane. A graphite rod of 0.5 cm diameter and 2.5 cm length and a 2 cm x 3 cm copper sheet were used as the anode and the cathode, respectively. Highly purified butadiene was bubbled into the anolyte during electrolysis in order to keep the concentration of butadiene in the anolyte at a constant value, 2 mol dm<sup>-3</sup>. Acetonitrile (MeCN) was dried with molecular shieves 5A and CaH2, and then distilled twice. Butadiene and its derivatives were determined by gaschromatography combined with mass-spectrometry. The mixed solution of the anolyte and the catholyte was analyzed in the same way. Chloride ion was determined by the Volhard method. All electrolyses were performed at 25 °C.

Table 1 presents the experimental conditions and the current efficiencies for the formation of the dichlorobutenes in two typical runs. No appreciable amounts of such butadiene derivatives other than 3,4-DCB and trans-1,4-DCB as cis-1,4dichloro-2-butene or 4-vinyl-1-cyclohexene were detected on the gaschromatograms. The current efficiency for each dichlorobutene is defined as the percentage of the quantity of electricity used for the formation of the dichlorobutene against the quantity of electricity that passed through the cell, and was calculated by assuming that the chlorination was a two-electron reaction. The quantity of electricity passed in run (a), 482 C, is that required to convert ca. 4% of buta-

	Separator	Electrolyte		Electricity	Current/A		Current efficiency/%	
		Anolyte	Catholyte	passed/C	Initial	Final	3,4-DCB	trans-1,4-DCB
(a)	Glass frit	CoCl <sub>2</sub> -MeCN (30 ml)	CoCl <sub>2</sub> -MeCN (30 ml)	482	0.10	0.02	40	51
(b)	Anion <del>-</del> exchange membrane	CoCl <sub>2</sub> -MeCN (40 ml)	NH <sub>4</sub> Cl-H <sub>2</sub> O (40 ml)	482	0.16	0.03	46	52

Table 1. Electrolytic conditions and current efficiencies for the formation of dichlorobutenes

 $[C_4H_6] = 2 \mod dm^{-3}$ ,  $[CoCl_2] = 0.50 \mod dm^{-3}$ ,  $[NH_4Cl] = 1.0 \mod dm^{-3}$ , anode potential = 1.7 V vs Ag/AgCl.

diene initially dissolved in the anolyte  $(2 \text{ mol } dm^{-3})$  into dichlorobutenes. In both runs the total current efficiencies for the formation of 3,4-DCB and trans-1,4-DCB were higher than 90%. When the glass frit separator was used, the total current efficiency and the yields of trans-1,4-DCB to 3,4-DCB were respectively ca. 90% and 1.4. On the other hand, when the anion-exchange membrane was used, they were ca. 98% and 1.1. A separate experiment indicated that these differences can be attributed to the diffusion of the dichlorobutenes into the catholyte through the glass frit and the following preferential dechlorination of 3,4-DCB at the cathode.

In conclusion, butadiene can be electrochemically chlorinated at room temperature, by using an H-type cell with a  $CoCl_2$ -MeCN anolyte and an NH<sub>4</sub>Cl-H<sub>2</sub>O catholyte, to form 3,4-DCB and trans-1,4-DCB in high current efficiencies if the anolyte and catholyte are well-separated. The electrochemical chlorination is of greater dvantages than the usual chemical method, because it does not need the use of expensive and toxic chlorine or a high temperature.

## Reference

1). A.P. Tomilov, Yu.D. Smilnov, and Yu.I. Rozin, Zh. Obsch. Khim., 44, 2028 (1974).

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