CHEMISTRY LETTERS, pp. 1685-1686, 1981.

ELECTROCHEMICAL CHLORINATION OF BUTADIENE

Yoshio TAKASU*, Yoshiharu MATSUDA, Akinori SHIMIZU,
Masayuki MORITA, and Mitsutaka SAITO[†]
Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube 755
[†] Research Laboratory of Toyo Soda Manufacturing Company,
Tonda 4560, Shin-nanyo 746

An Electrochemical chlorination of butadiene was investigated at 25 °C by using an H-type cell with a $CoCl_2$-MeCN anolyte and an NH_4Cl-H_2O catholyte separated by an anion-exchange membrane. The electrolysis gave 3,4-dichloro-1-butene and trans-1,4-dichloro-2-butene in high current efficiencies.

3,4-Dichloro-1-butene (3,4-DCB) and trans-1,4-dichloro-2-butene (trans-1,4-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.$^{1)}$ 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^{-3}. Acetonitrile (MeCN) was dried with molecular shieves 5A and CaH_2, 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-1,4-dichloro-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-

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

	Separator	Electrolyte		Electricity passed/C	Current/A		Current efficiency/%	
		Anolyte	Catholyte		Initial	Final	3,4-DCB	trans-1,4-DCB
(a)	Glass frit	$CoCl_2$-MeCN (30 ml)	$CoCl_2$-MeCN (30 ml)	482	0.10	0.02	40	51
(b)	Anion-exchange membrane	$CoCl_2$-MeCN (40 ml)	NH_4Cl-H_2O (40 ml)	482	0.16	0.03	46	52

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

diene initially dissolved in the anolyte (2 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_4Cl-H_2O 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).

(Received August 22, 1981)