Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 1099–1101. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1165–1167.
Original Russian Text Copyright © 2001 by Tomilov.

Cathodic Dehalogenation with Dimerization. Dimerization in the Course of Reduction of Butyl Iodide

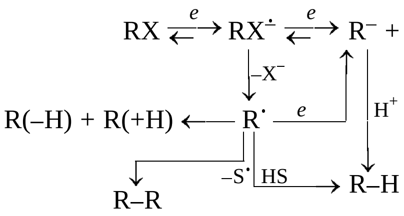
A. P. Tomilov

State Research Institute of Organic Chemistry and Technology, Moscow, Russia

Received January 17, 2000

Abstract—Electrochemical reduction of butyl iodide in methanol with a sodium methylate supporting electrolyte was studied. The yield of the dimeric product, octane, largely depends on the cathode material, with copper and iron (St.3 steel) being the most active. At a current density of 0.03–0.10 A cm^{-2}, 0°C, and 0.005 M CH_3ONa, the yield of octane, based on butyl iodide, is as high as 83–84%.

According to modern data [1], the general scheme of cathodic reduction of organic halides can be presented as follows:



where X is halogen and HS is solvent.

According to this scheme, the major reduction pathways are substitution of hydrogen for halogen and dimerization of the free radicals. The latter pathway is an electrochemical analog of the well-known Würtz reaction [2] and is of certain practical interest. At the same time, data on formation of dimeric products in the course of electrolytic reduction of organic halides are scarce. For example, reduction of methylene iodide in aqueous alcohol gave ethylene in a ~30% yield [3]:

$$2CH_2I_2 + 4e \longrightarrow CH_2{=}CH_2 + 4I^-.$$

Reduction of butyl iodide gave butane in approximately the same yield [4, 5]:

$$2C_2H_5I + 2e \longrightarrow C_4H_{10} + 2I^-.$$

The formation of acetylene compounds in the course of reduction of 1,1,1-trichloro-2,2-diphenylethane and its derivatives was reported in [6–8]:

$$2Ar_2CHCCl_3 + 6e \longrightarrow Ar_2CHC{\equiv}CCHAr_2 + 6Cl^-.$$

Dimerization of 1-cyano-2-iodoethane gave adipodinitrile in a ~6.5% yield [5]:

$$2ICH_2CH_2CN + 2e \longrightarrow NC(CH_2)_4CN + 2I^-.$$

The dimeric product can also be obtained by reduction of bromoethyl acetate [9]:

$$BrCH_2CH_2OOCCH_3 + 2e$$
$$\longrightarrow CH_3COO(CH_2)_4COOCH_3 + 2Br^-.$$

We found no papers devoted to optimization of electrolytic reductive dimerization of organic halides. The above scheme suggests that, to increase the yield of the dimeric product, the process should be performed at a cathode potential as low as possible, so as to minimize further reduction of the R$^·$ radical to the R$^-$ anion.

Preliminary voltammetric studies showed that the reduction potential of organic halides appreciably depends on the cathode material [10]. For example, in reduction of ethyl bromide the lowest reduction potential was observed with a copper cathode, especially with that coated with spongy copper. Therefore, our work on optimization of dimerization by dehalogenation was started with testing of various cathode materials. As a model compound we chose butyl iodide.

The first series of experiments was aimed at revealing the effect of the cathode material on the selectivity of butyl iodide reduction. The major attention was given to pretreatment of the electrode surface before each run. Metallic cathodes were etched for a short time in 5% HCl, washed, wiped with sodium carbonate, and rinsed with distilled water. If spots or streaks appeared on the electrode surface, the etching was repeated. The results of the experiments are listed in Table 1. All experiments were performed at a sodium methylate concentration of 0.005 M, which was suffi-

1070-3632/01/7107-1099 $25.00 © 2001 MAIK "Nauka/Interperiodica"

Table 1. Effect of cathode material on reduction of butyl iodide in methanol[a]

Cathode material	Yield as a function of current, %			Yield of octane based on butyl iodide, %
	H_2	C_4H_{10}	C_8H_{18}	
Pb	28	29.6	–	–
Zn	27	72.2	–	–
Hg	4	36.0	–	–
Sn	29	30.1	14.8	47.8
Graphite	31	34.0	17.3	56.0
Cu	21	25.7	45.6	79.6
St.3 steel	34	19.6	37.5	78.0
Ni	50	24.7	18.8	60.0

[a] Catholyte 0.005 M CH_3ONa in methanol (270 ml), 50 g of butyl iodide; current density 0.028 A cm^{-2}; temperature 20–25°C.

Table 2. Effect of sodium methylate concentration on reduction of butyl iodide[a]

$[CH_3ONa]$, M	Obtained, g		Yield of octane based on butyl iodide, %
	C_4H_{10}	C_8H_{18}	
0.005	2.3	9.2	78.0
0.05	4.15	7.7	64.5
0.20	7.9	6.0	42.6
0.35	5.9	5.7	49.1
0.70	5.1	5.1	48.9

[a] The other conditions are the same as for Table 1.

cient to ensure the conductivity required for preparative electrolyses. Preliminary experiments showed that in methanolic solutions of sodium methylate of the concentration up to 0.7 M butyl iodide is not noticeably saponified at room temperature. Experiments with lead, mercury, tin, and zinc cathodes showed that these cathodes degrade under the process conditions. From the solution obtained by electrolysis with a lead cathode, we isolated and identified tributyllead iodide Bu_3PbI (found, %: C 28.6; H 5.55; I 25.0. $C_{12}H_{27}PbI$. Calculated, %: C 27.9; H 5.30; I 24.0). Similar organometallic compounds can be expected to form with the other degradable cathodes, but we did not isolate and identify them. Table 1 shows that the best yields are attained with copper and iron cathodes. However, the reduction on iron is slower than on copper, as judged from the higher yield of hydrogen on the iron cathode. The high yield of butane on the zinc cathode is probably due to the fact that reduction is partially due to chemical dissolution of zinc. Data in Table 1 refer to a smooth copper cathode. For comparison, we performed an experiment under the same conditions with a cathode coated with spongy copper. On such an activated electrode no hydrogen evolution was observed in the first 1.5 h of the electrolysis, i.e., reduction occured at a high rate; however, the yield of octane based on butyl iodide was essentially the same, 80.1%. Further experiments showed that variation of the current density in the range 0.03–0.10 A cm^{-2} has no appreciable effect on the reduction, whereas, as the sodium methylate concentration is increased from 0.005 to 0.7 M, the process parameters become worse (despite somewhat lower working voltage on the electrolyzer), which is illustrated in Table 2. The yield of octane increases as the temperature is decreased to 0°C. In the experiment performed at 0–1°C, the yield of octane based on butyl iodide was 83–84%.

Thus, dimerization of butyl iodide by cathodic dehalogenation can be performed with a good yield. The copper cathode shows a high electrocatalytic activity; the dimeric product can also be obtained with an iron cathode.

EXPERIMENTAL

Chemically pure grade butyl iodide was distilled prior to use; the fraction with bp 101–102°C was collected. Chemically pure grade methanol was used as solvent without additional purification. Solution of sodium methylate was prepared by dissolution of the calculated amount of metallic sodium in methanol.

Experiments were performed in a cylindrical glass electrolyzer equipped with a cooling jacket. The cathodic and anodic compartments were separated with a ceramic diaphragm (Fig. 4 in [11]). The volume of the cathodic compartment was 300 ml, and the cathode surface area, 60 cm^2. The solution was stirred with a power-driven stirrer.

Gaseous electrolysis products passed through a trap cooled with an acetone–dry ice mixture. Butane condensed in the trap. Hydrogen was collected in a Mariotte vessel. After electrolysis completion, the catholyte was diluted with a threefold amount of water to separate crude octane, which was dried and analyzed chromatographically.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 97-03-32265).

REFERENCES

1. Kyriacou, D., *Modern Electroorganic Chemistry*, Berlin: Springer, 1994.
2. Vatsuro, K.V. and Mishchenko, G.L., *Imennye reaktsii* (Named Reactions), Moscow: Khimiya, 1976, p. 128.
3. Andryushchenko, K.V. and Orlova, V.V., *Ukr. Khim. Zh.*, 1962, vol. 28, no. 3, pp. 268–270.
4. Plump, R. and Hammett, L., *Trans. Electrochem. Soc.*, 1938, vol. 23, pp. 523–529.
5. Feoktistov, L.G., Tomilov, A.P., Smirnov, Yu.D., and Gol’din, M.M., *Elektrokhimiya*, 1965, vol. 1, no. 8, pp. 887–893.
6. Brand-Giessen, K., *Z. Elektrochem.*, 1910, vol. 16, no. 16, pp. 669– 672.
7. Brand, K. and Masui, M., *Ber.*, 1913, vol. 46, no. 3, pp. 2942–2949.
8. Brand, R. and Kricke-Amelung, D., *Ber.*, 1939, vol. 72, no. 5, pp. 1029–1047.
9. Chipris, D., *J. Electrochem.*, 1978, vol. 8, no. 6, pp. 537–544.
10. Tomilov, A.P., Turygin, V.V., and Khudenko, A.V., *Zh. Prikl. Khim.*, 1999, vol. 72, no. 2, p. 329.
11. Tomilov, A.P. and Kirilyus, I.V., *Katodnye sintezy organicheskikh preparatov* (Cathodic Syntheses of Organic Compounds), Alma-Ata: Nauka, 1982.