Russian Journal of Applied Chemistry, Vol. 74, No. 8, 2001, pp. 1318–1320. Translated from Zhurnal Prikladnoi Khimii, Vol. 74, No. 8, 2001, pp. 1281–1284.
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SORPTION AND ION-EXCHANGE PROCESSES

Electrochemical Methoxylation of Styrene with Gas-Lift in Continuous Mode

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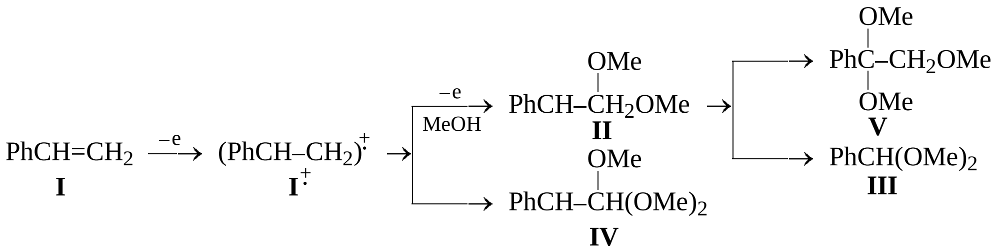
Received February 14, 2001

Abstract—Anodic oxidation of styrene in methanol was performed in an electrolyzer with gas-lift. The possibility of carrying this process out in continuous mode with the use of technical-grade methanol was studied.

Recently, the reaction of styrene methoxylation, making possible manufacture of a number of important organic preparations, e.g., benzaldehyde and anisaldehyde, has been studied intensively. Electrochemical methoxylation of styrene (**I**) leads to formation of 1,2-dimethoxyethylbenzene (**II**) with subsequent splitting of the C–C bond and conversion of **II** into dimethylacetal of benzaldehyde (**III**):



$$\underset{\mathbf{I}}{PhCH{=}CH_2} \xrightarrow{-e} \underset{\mathbf{I}^{\dot{+}}}{(PhCH{-}CH_2)^{\dot{+}}} \rightarrow \begin{cases} \xrightarrow[MeOH]{-e} \underset{\mathbf{II}}{PhCH{-}\overset{OMe}{CH_2OMe}} \rightarrow \begin{cases} \rightarrow \underset{\mathbf{V}}{PhC(OMe)_2{-}CH_2OMe} \\ \rightarrow \underset{\mathbf{III}}{PhCH(OMe)_2} \end{cases} \\ \rightarrow \underset{\mathbf{IV}}{PhCH(OMe){-}CH(OMe)_2} \end{cases}$$

A number of studies have been concerned with the effect of a supporting electrolyte, anode material, and other factors on the yield of the reaction products [1–5]. It was established that conversion of styrene **I** into 1,2-dimethoxyethylbenzene **II** is the most efficient in electrolysis with a platinum anode and potassium fluoride solution as supporting electrolyte. The conditions were described under which the yield of compound **III** is as high as 66%, and the current efficiency, 33%, after passing 8 F of electricity per 1 mol of styrene.

All the experiments described in the literature have been performed in a diaphragmless glass electrolyzer equipped with magnetic stirrer for solution agitation. Such an electrolyzer cannot serve as a prototype of an industrial apparatus.

In the industry, the best-developed design is the electrolyzer of filter-press type in which the electrolyte circulation is effected by gases formed in electrolysis—the gas-lift system [6]. Electrolyzers of this kind exhibit good performance in electrolysis of water. It has been shown that cathodic hydrodimerization of acetone can be performed in an electrolyzer with gas-lift system [7].

Electrochemical synthesis of compound **III** is of practical importance. In view of this fact, the present study was aimed at verifying the possibility of carrying out the given reaction in a prototype industrial electrolyzer. In order to create conditions as close as possible to those used in the industry, the process was performed in continuous mode with the use of technical-grade methanol [GOST (State Standard) 2222–95] as solvent.

EXPERIMENTAL

The experiments were carried in electrolyzer *1* (see figure) in the form of a glass cylinder 55 mm in diameter and 140 mm high. An electrode pack compris-

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ing alternating anode and cathode plates was placed inside the electrolyzer. Two platinum plates of size 15 × 80 mm were used as anode, and three stainless steel plates of the same size, as cathode. The interelectrode spacing of 3 mm was ensured by fluoroplastic spacers placed at electrode edges. The installation is shown schematically in the figure. The ascending pipe of the gas-lift system had inner diameter of 6 mm and height of 1650 mm. The capacity of the whole system was 420 ml. The current density was calculated on the assumption of the uniform distribution of current over the entire surface of the cathodes.

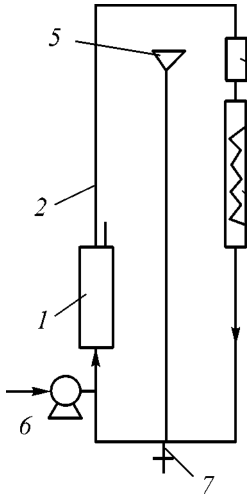
A 20.8-g portion of styrene (0.2 mol), 1.4 g (0.02 mol) of KF, and 397 ml of methanol was placed in the system, so that it was filled to the level shown in the figure. The electrolysis was carried out at a current density of 0.1 A cm^{-2} (current strength 4.8 A), with 8 F of electricity passed per 1 mol of styrene **I** and no fresh electrolyte added. The voltage across the electrolyzer was 10 V.

After the electrolysis was complete, methanol was evaporated under a water-jet pump vacuum at a temperature of 40°C, still bottoms were extracted with hexane (20 × 3), and the solvent was evaporated from the extract. The still bottoms were weighed and analyzed by liquid-gas chromatography on an LKhM-8MD chromatograph (detector catharometer, carrier-gas helium, column length 1.5 m, column diameter 3 mm, support Chromaton-N-AW, immobile phase PEG-4000, flow rate 4 ml s^{-1}, sensitivity 1 : 3, column temperature 130°C, evaporator temperature 250°C).

For comparison, experiments were performed in an electrolyzer with magnetic stirrer, with design close to that described in [1–5].

Table 1 presents data on the accumulation of electrolysis products both in an electrolyzer with gas-lift and in that with mechanical stirring. It can be seen that the yield of benzaldehyde dimethylacetal **III** is nearly 14% higher in the electrolyzer with a gas-lift system, compared with that equipped with mechanical stirrer.

Further experiments were carried out in order to verify the possibility of performing the process in the continuous mode. A certain amount of electrolyte solution was removed from the electrolyzer every hour and a fresh portion of the same volume was added. Two sets of experiments were carried out with fresh electrolyte supplied at a rate of 25 ml h^{-1}.



Electrolyzer with gas-lift system. (*1*) Electrolyzer, (*2*) glass tube, (*3*) condenser, (*4*) separator, (*5*) system filling level, (*6*) dosing pump, and (*7*) discharge cock.

The yield of the reaction products was found not to change substantially on passing from batch to continuous mode (Table 2). Also, the possibility was verified of conversion of the intermediate electrolysis product—1,2-dimethoxyethylbenzene, in an electrolyzer of continuous type with gas-lift. In this case, one more product of the reaction of electrochemical methoxylation of styrene—1,1,2-trimethoxyethylben-

Table 1. Electrooxidation of styrene in methanol in batch mode in electrolyzers with (A) mechanical stirring and (B) gas-lift

Quantity of electricity, F mol^{-1}	Composition of electrolysis products, %				
	(I)	**(II)**	**(III)**	**(IV)**	BA
	Electrolyzer (A)*				
1	20	73.2	4.4	1.9	1
2	12	76.5	7.4	2.3	2
3	–	87.5	7.9	2.6	2
4	–	74.2	16.8	7	2
5	–	67.7	20.9	8.4	3
6	–	59.5	29.1	8.5	3
7	–	54.7	33.6	8.7	3
8	–	39	42.8	13	5
	Electrolyzer (B)				
1	25	65.5	6.9	1.6	1
2	18.3	68.9	7.6	3.2	2
3	9.7	70.7	11.1	5.5	3
4	–	71	20	6	3
5	–	66.7	29.8	6.5	3
6	–	56	32	8	4
7	–	45.3	41.8	8.9	4
8	–	30	57	9	4

* Electrolysis conditions: 10.4 g (0.06 mol) styrene, 0.7 g (0.01 mol) KF, and 185 ml methanol; *T* = 60°C; BA, benzaldehyde.

Table 2. Electrooxidation of styrenes in electrolyzer with gas-lift system in continuous mode (fresh solution supplied at a rate of 25 ml h^{-1})

τ, h	Composition of electrolysis products, %									
	II	**III**	**IV**	**V**	BA	**II**	**III**	**IV**	**V**	BA
	Styrene					1,2-Dimethoxyethylbenzene**				
9	30	56	10	–	4	30	57	10	–	4
17*	31	55	10	–	5	10	57	10	18	5
25*	30	55	10	–	5	8	56	10	21	5
33*	31	54	10	–	5	8	56	10	21	5
41*	30	55	10	–	5	7	56	10	22	5

* Addition of fresh electrolyte (styrene) was started after passing 8 F of electricity per 1 mol of styrene.

** Fresh electrolyte: 12 g (0.06 mol) of 1,2-dimethoxyethylbenzene, 0.7 g of KF, and 200 ml of methanol.

Table 3. Electrooxidation of styrene in methanol in continuous mode (fresh electrolyte supplied at a rate of 50 ml h^{-1})

τ, h	Composition of electrolysis products, %				τ, h	Composition of electrolysis products, %			
	II	**III**	**IV**	BA		**II**	**III**	**IV**	BA
i = 0.1 A cm^{-2}					i = 0.2 A cm^{-2}				
9	30	55	10	5	4.5	30	56	10	4
17*	44	39	11	6	12.5*	40	45	10	5
25*	46	38	10	6	20.5*	40	44	10	6
33*	46	37	11	6	28.5*	39.5	43.5	11	6
41*	44	39	11	6	36.5*	39	44	11	6

* Addition of fresh electrolyte (styrene) was started after passing 8 F of electricity per 1 mol of styrene.

zene (**V**), is formed in yield of up to 18–22% in a continuous-type electrolyzer with gas-lift and 10% in an electrolyzer with mechanical stirring [5].

A set of experiments carried out with varied current density at a supply rate of fresh electrolyte of 50 ml h^{-1} demonstrated that the yield of the target product grows with the current density increasing to 0.2 A cm^{-2} (Table 3).

Tables 1–3 present the results averaged over three measurements. The relative error of the average is 1.6% at confidence probability $\alpha = 0.95$.

The obtained data indicate that in an electrolyzer with gas-lift system, operating in the continuous mode, the process course is stable, with lower electrolyte supply rate ensuring higher yield of product **III**, virtually coinciding with that achieved in the batch mode.

CONCLUSION

Methoxylation of styrene to obtain benzaldehyde dimethylacetal can be carried out in continuous mode in an electrolyzer with electrolyte circulation effected by gas-lift.

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