The effect of electrolysis conditions on the oxidation of styrene in methanol

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Anodic oxidation of styrene (1) in methanol and the effect of the anion of the supporting electrolyte and of the anode material on this process have been studied. The most efficient conversion of 1 into (1,2-dimethoxyethyl)benzene (2) occurs when the electrolysis is carried out with a platinum anode and with potassium fluoride or tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Cleavage of the C—C σ bond in 2 to give benzaldehyde dimethylacetal (3) is the most efficient at a graphite anode in the presence of sodium tosylate.

Key words: styrene, anodic oxidation, electrochemical cleavage of carbon—carbon π and σ bonds; (1,2-dimethoxyethyl)benzene; benzaldehyde dimethylacetal; (1,1,2-trimethoxyethyl)and (1,2,2-trimethoxyethyl)benzenes.

In a continuation of our investigations on electrochemical cleavage of benzyl carbon—carbon π and σ bonds in arylaliphatic compounds,¹⁻³ in the present work we studied the effect of supporting electrolytes and anode materials on these processes using the anodic oxidation of styrene (1) as an example.

It has been found previously that the cleavage of the C=C bond in 1 results from the oxidation of molecules 1 adsorbed on the anode and subsequent solvolysis of the intermediates formed. As this takes place, compound 1 is converted into (1,2-dimethoxyethyl) benzene^{4,5} (2) (Scheme 1).

Scheme 1 $(PhCH=CH_2)_{ad} \xrightarrow{-e} (PhCH-CH_2)_{ad}^{+} \xrightarrow{-e/MeOH}$ $1 \qquad 1^{+} \xrightarrow{OMe}$ $PhCHCH_2OMe$ 2

Electrolysis of product 2 is accompanied by cleavage of the C–C bond to afford benzaldehyde dimethylacetal² (3) (Scheme 2).

These reactions result in the complete cleavage of the C=C bond in styrene.

In the present work we studied the effect of the anions of supporting electrolytes and the anode material on the electrochemical cleavage of carbon—carbon π





and σ bonds in arylaliphatic compounds using anodic oxidation of compound 1 in methanol as an example. We studied the two processes (see Schemes 1 and 2) carried out separately and also the direct conversion of 1 into acetal 3.

We used platinum and graphite anodes and tetrabutylammonium perchlorate, tetrabutylammonium tetrafluoroborate (TBAF), potassium fluoride, sodium toluene-p-sulfonate, and sodium dibutyl phosphate as supporting electrolytes. Electrolysis was carried out in a undivided cell under galvanostatic conditions in 0.1 Msolutions of electrolytes in methanol at 60 °C, at an initial concentration of substrates of 0.5 mol L^{-1} , and a current density of 100 mA cm⁻². In the oxidation of 1 to 2, 2 F of electricity per mole of the substrate was passed through a solution; in the oxidation of 2 to 3 and of 1 to 3, 6 and 8 F per mole of the substrate, respectively, was passed. Table 1 presents the results of the oxidation of compound 1. The best results in the oxidation of compound 1 to 2 were obtained with a platinum anode and with potassium fluoride or TBAF as the

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 1624-1628, September, 1994.

Run	Supporting electrolyte ^b	Anode	Quantity of electricity, $Q/F \text{ mol}^{-1}$	Degree of conversion 1 (%)	Yield of the electrolysis products (%, theoretical) ^c			
					2	3	5	6
1	KF	Pt	2	90	80	1	5	3
2	KF	С	2	90	66	7	5	6
3	KF	С	8	100	8	64		4
4	TBAF	Pt	2	93	76	1	4	2
5	TBAF	С	2	78	54	18	3	6
6	TFA	Pt	2	51	71		2	4
7	TFA	С	2	80	59	6	5	8
8	TFA	С	8	100	15	61		3
9	TOS	Pt	2	60	67	1	5	1
10	TOS	С	2	68	63	10	4	4
11	TOS	С	8	100	3	66		4
12	TPC	Pt	2	79	66	4	2	2
13	TPC	С	2	92	45	16	2	13
14	DBP	Pt	2	67	55		3	3
15	DBP	С	2	92	63	4	7	7

Table 1. Electrooxidation of styrene (1) in methanol using of various supporting electrolytes and anode materials^a

^{*a*} Electrolysis conditions: 30 mL of a solution containing 15 mmol of **1** and 3 mmol of a supporting electrolyte in methanol; 60 °C; stainless-steel cathode; current density 100 mA cm⁻². ^{*b*} TBAF is tetrabutylammonium tetrafluoroborate, TFA is sodium trifluoroacetate, TOS is sodium tosylate, TPC is tetrabutylammonium perchlorate, DBP is sodium dibutyl phosphate. ^{*c*} Minor amounts of 1,4-dimethoxy-2,4-diphenylbutane (**8**) and 1,4-dimethoxy-2,3-diphenylbutane (**9**) (~2 %) formed in runs 1, 4, 6, 9, 12, and 14; 2 % of (1,1,2-trimethoxyethyl)benzene (**11**) formed in runs 3, 8, and 11, and ethylbenzene (1-4 %) was obtained in all of the runs.

supporting electrolyte (the degree of conversion of 1 was 90-93 %, the yield of 2 was 76-80 %). In the case of a graphite anode and potassium fluoride, the degree of conversion of 1 was the same, but the yield of compound 2 was lower (see Table 1, run 2), and in the presence of TBAF, the degree of conversion also decreased, though the yield of acetal 3 substantially increased (run 4). In addition to compounds 2 and 3, (1,2,2-trimethoxyethyl)benzene (5) (2-7%), 1,4-dimethoxy-1,4-diphenylbutane (6) (1-13%), 1,4-dimethoxy-2,3-diphenylbutane (9), and ethylbenzene (1-4%) were obtained in all cases.

The formation of compound **5** is probably due to the competing conversion of the electrically generated radical cations 1^{+} into β -methoxystyrene (**4**) followed by methoxylation of the latter (Scheme 3).

Scheme 3



Addition of radical cations 1^{+} to styrene and their recombination 4^{-6} afford dimer 6 (Scheme 4).

Scheme 4



The dimeric products 8 and 9 (Scheme 5) are formed only during electrolysis with a platinum anode. Most likely, they result from the electrical generation of methoxyl radicals on platinum,^{7,8} their subsequent addition to molecules 1, and recombination of radicals 7 with 1^+ or with one another.

The results obtained indicate that the electrochemical behavior of compound 1 in its anodic oxidation with various supporting electrolytes and at platinum and graphite anodes is different, as has also been noted previously.^{4,5,9} It is believed that this is determined by the adsorption properties of the anodes and the different absorption abilities of the substrate molecules, solvent molecules, and electrolyte anions. The higher the adsorption of the substrate, the more actively it is involved in the electrochemical process. Under comparable conditions, styrene is more efficiently adsorbed on graphite



than on platinum, judging by the degree of its conversion in the presence of the majority of the electrolytes used. TBAF was an exception: in its presence, the opposite situation was observed, *i.e.*, the degree of conversion decreased by 15 % (see Table 1, run 5). At the same time, the conversion of compound 2 into acetal 3 was the most active in this run, resulting in a competing consumption of electricity by this side reaction and, as a consequence, in a decrease in the conversion of 1. On the other hand, the formation of substantial amounts of compound 3 points to the fact that tetrafluoroborate anions, like perchlorate anions,⁴ displace compound 2 from the graphite surface to a lesser extent and thus favor its oxidation to acetal 3.

Thus, the electrochemical conversion of 1 into 2 occurs most efficiently at a platinum anode in the presence of potassium fluoride or TBAF as the supporting electrolyte. Under these conditions, compound 2 was obtained in a 76-80 % yield at a conversion of 90-93 %, whereas in the presence of sodium methoxide the yield did not exceed 20 % (see Ref. 8, 9), and it amounted to 36 % in the case of tetraethylammonium perchlorate.⁹

Table 2 presents the data on the effects of the anions of the supporting electrolytes and the anode materials on the electrochemical cleavage of the benzyl C--C σ -bond of compound 2. It was found that in most of the experiments, in addition to acetal 3, (1,1,2trimethoxyethyl)benzene (11) (yield 2--12 %) is formed. Compound 11 results from the oxidation of radicals 10 generated by fragmentation of radical cations 2⁺ · with elimination of a proton,^{10,11} and by the abstraction of the α -H atoms from compound 2 by methoxyl radicals during anodic oxidation of 2 at a platinum anode, as indicated by the fact that at a platinum anode the yield of 11 is twice as high as at a carbon anode (Scheme 6).



Table 2. Electrooxidation of (1,2-dimethoxyethyl) benzene (2) in methanol with platinum and graphite anodes in the presence of various supporting electrolytes

Run	Supporting electrolyte	Anode	Conversion 2 (%)	Yield of the electrolysis products (%, theoretical)		
			_	3	11	
1	KF	Pt	72	82	10	
2	KF	С	85	75	4	
3	TBAF	Pt	66	86	5	
4	TBAF	С	98	73		
5	TFA	Pt	66	79	12	
6	TFA	С	70	84	4	
7	TOS	Pt	55	87	4	
8	TOS	С	87	83	2	
9	TPC	Pt	76	80	8	
10	TPC	С	96	70	_	
11	DBP	Pt	52	79	10	
12	DBP	С	87	76	5	

Note: 6 F mol⁻¹ of electricity was passed; for the other electrolysis conditions, see Table 1.

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The optimum results of the conversion of 2 (87 %) and the yield of 3 (83 %) were achieved with a graphite anode in the presence of sodium tosylate (see Table 2, run 8). With a platinum anode in the presence of potassium fluoride or TBAF as the supporting electrolyte, *i.e.*, under the conditions where electrolysis of **1** would have given the best results with respect to the conversion of 1 and the yield of 2, the electrochemical cleavage of the benzyl C-C bond occurs with lower degrees of conversion (66-72 %), but with similar yields of 3 (82-86%). The different effects of the nature of the electrolyte anion and of the anode material on the anodic oxidation of compounds 1 and 2 can be explained by the more efficient adsorption of substrates on graphite. The tetrafluoroborate and perchlorate anions of the supporting electrolyte favor this to a greater extent than the tosylate ions. Consequently, molecules of the solvent are partially displaced from the graphite surface, and this leads to a decrease in the consumption of electricity by the side process of oxidation that makes it necessary to pass three times as much electricity (with respect to the theoretical amount, 2 F mol^{-1}), in order to achieve a high degree of conversion of 2 and 3. In addition, due to the more active adsorption of aromatic substrates in the presence of tetrafluoroborate and perchlorate anions, the subsequent oxidation of acetal 3 occurs to a greater extent and, hence, its yield decreases.

The use of a graphite anode and of sodium tosylate as the supporting electrolyte makes it possible as well to carry out the most efficient cleavage of the benzyl carbon—carbon π and σ bonds in compound 1 in one process, *i.e.*, direct oxidation of 1 to 3 (see Table 1, runs 3, 8, and 11).

Thus, as a result of the study of the effect of the nature of the anions of supporting electrolytes and anode materials on the electrochemical cleavage of the π and σ benzyl carbon—carbon bonds of styrene, we determined the conditions for the most efficient realization of these reactions as two separate steps and as one process.

Experimental

GLC analysis was carried out on a Varian-3700 chromatograph with a flame ionization detector in a flow of nitrogen (30 mL min⁻¹) using 200×0.3 cm glass columns with 5 % Carbowax 20M on Inerton N-AW (0.15–0.20 mm) and with 5% XE-60 on Chromaton N-AW (0.125–0.160 mm). ¹H and ¹³C NMR spectra (in CDCl₃) were recorded on Jeol FQ-90Q, Bruker WM-250, and Bruker AM-300 spectrometers; mass spectra were obtained on Varian MAT CH-6 and Varian MAT CH-111 instruments (70 eV) with chromatographic injection of samples.

Commercial styrene of the "pure" grade was distilled prior to use. Sodium tosylate, sodium trifluoroacetate, and potassium fluoride of the "pure" grade were used. Tetrabutylammonium perchlorate and tetrafluoroborate were prepared by the reaction of NH_4ClO_4 and $NaBF_4$, respectively, with tetrabutylammonium bromide. Sodium dibutyl phosphate was obtained by neutralization of dibutyl phosphate (of the "pure" grade) with sodium bicarbonate. All of the supporting electrolytes were dried over P_2O_5 prior to use. Methanol was dehydrated by distillation over magnesium methoxide.

Electrochemical synthesis of (1,2-dimethoxyethyl)benzene (2) from styrene (1). Compound 1 (20.8 g, 0.2 mol), 370 mL of methanol, and KF (1.3 g) were placed into a 500-mL temperature-controlled electrolyzer equipped with a platinum anode (a 50×15 mm plate), a steel cathode (a 50×15 mm stainless-steel plate), reflux condenser, and a magnetic rod for stirring. Electrolysis was carried out at 60 °C, at a current density of 100 mA cm⁻², and with efficient stirring. 2 F of electricity per mole of 1 were passed. The methanol was evaporated, the residue was extracted with hexane $(2 \times 50 \text{ mL})$, and the extract was concentrated. Fractional distillation in vacuo gave 21 g (65 %) of compound 2, b.p. 108–110 °C (18 Torr), $n_{\rm D}^{20}$ 1.5007 (cf. Refs. 8, 9). ¹H NMR, 8: 3.29 (s, 3 H); 3.40 (s, 3 H); 3.42 (dd, 1 H, J = 7.3 and 2.4 Hz); 3.58 (dd, 1 H, J = 7.3 и 5.5 Hz); 4.39 (m, 1 H); 7.23-7.40 (m, 5 H). 13 C NMR, δ : 138.87 (s); 128.54 (d); 128.10 (d); 127.01 (d); 83.02 (d, CH); 77.36 (t, CH₂); 59.28 and 57.02 (both q, OMe). MS (EI), m/z (I_{rel} (%)): 166 [M⁺] (1.4), 135 (1.5), 134 (2.4), 122 (13.8), 121 (100), 105 (6.3), 91 (17.4), 77 (19.4).

Anodic oxidation of 1 and 2 (general procedure). Electrochemical oxidation was carried out under galvanostatic conditions in a 40-mL temperature-controlled cell equipped with a platinum anode (50×15 mm plate) or a graphite anode (a rod of diameter 8 mm), a stainless-steel cathode (a 50×15 mm plate) (the distance between the electrodes was 3 mm), a thermometer, a reflux condenser, and a magnetic rod to stir the contents of the cell. Conditions of the electrolysis: 0.5 mol L^{-1} of 1 or 2 and 0.1 mol L^{-1} of a supporting electrolyte; current density 100 mA cm⁻², 60 °C, efficient stirring. In the electrooxidation of 1, 2 F mol⁻¹ (see Table 1, all of the runs except for 3, 8, and 11) or 8 F mol⁻¹ (runs 3, 8, and 11) of electricity were passed; in the oxidation of 2, 6 F mol⁻¹ were passed. The reaction mixture was analyzed by GLC using reference compounds and an internal standard (dodecane). The results of the analysis are presented in Tables 1 and 2.

In order to isolate and identify the products of the electrolysis, the reaction mixture was concentrated on a rotary evaporator, the residue was extracted with hexane $(2 \times 20 \text{ mL})$, the extract was concentrated, and the residue was chromatographed on SiO₂ using a hexane—ether mixture (20 : 1) as the eluent to give compounds 2, 3, 5, 6, 9, and 11.

(1,2-Dimethoxyethyl)benzene (2) was identical to the abovedescribed product.

Benzaldehyde dimethylacetal (3) was identical to the product obtained previously.²

(1,2,2-Trimethoxyethyl)benzene (5) (see Ref. 12). ¹H NMR, δ : 3.21 (s, 3 H); 3.26 (s, 3 H); 3.47 (s, 3 H); 4.19 and 4.38 (both d, 2 H, J = 8.1 Hz); 7.30–7.42 (m, 5 H). ¹³C NMR, δ : 138.02 (s); 128.31 (d); 128.08 (d); 106.50 (d, CH(OMe)₂); 83.90 (d, CH); 57.02, 55.76, and 54.40 (all q, OMe). MS, m/z (I_{rel} (%)): 165 [M⁺-OMe] (6), 164 (2.6), 121 (15.9), 105 (11.2), 91 (11.6), 77 (7.3), 75 [M⁺-PhCHOMe] (100).

1,4-Dimethoxy-1,4-diphenylbutane (6) (see Ref. 6). B.p. 133 °C (0.1 Torr), m.p. 66 °C (from hexane). ¹H NMR, δ : 1.56–2.05 (m, 4 H); 3.21 (s, 6 H); 4.10 (t, 2 H); 7.26–7.40 (m, 10 H). ¹³C NMR, δ : 142.30 (s); 142.19 (s); 128.38 (d); 127.49 (d); 126.71 (d); 126.63 (d); 84.05 and 83.83 (both d, CH); 56.61 (q, OMe); 34.78 and 34.18 (both t, CH₂). MS, *m/z* (I_{rel} (%)): 270 [M⁺] (0.3), 240 (3), 239 (6), 238 (25), 207 (8),

206 (9), 205 (7), 135 (6), 134 (30), 133 (8), 122 (10), 121 (100), 91 (7), 77 (10).

meso-1,4-Dimethoxy-2,3-diphenylbutane (9) (see Ref. 8). M.p. 131.5–132.5 °C (from hexane). ¹H NMR, δ : 3.12 (s, 6 H); 3.18 (m, 2 H); 3.34 (m, 4 H); 7.22–7.42 (m, 10 H). ¹³C NMR, δ : 48.59 (CH); 58.84 (OCH₃); 75.13 (CH₂); 126.69, 128.43, 128.52, and 142.29 (C₆H₅). MS, *m/z* (*I*_{ref} (%)): 270 [M⁺] (0.2), 238 (18), 206 (22), 193 (19), 169 (17), 135 (100), 134 (60), 121 (32), 91 (70).

(1,1,2-Trimethoxyethyl)benzene (11) (see Ref. 13). ¹H NMR, δ : 3.19 (s, 3 H); 3.21 (s, 6 H); 3.63 (s, 2 H); 7.28–7.53 (m, 5 H). ¹³C NMR, δ : 139.71 (s); 128.05 (d); 127.20 (d); 103.40 (s); 74.99 (t, CH₂); 59.57 and 48.95 (both q, OMe). MS, *m/z* (*I*_{rel} (%)): 165 [M⁺-OMe] (25), 151 (100), 137 (18), 105 (70), 91 (63), 77 (60).

References

- Yu. N. Ogibin, M. N. Elinson, A. B. Sokolov, and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 494 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 432 (Engl. Transl.)].
- 2. Yu. N. Ogibin, A. B. Sokolov, A. I. Ilovaiskii, M. N.

Elinson, and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 644 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 561 (Engl. Transl.)].

- 3. Yu. N. Ogibin, A. I. Ilovaiskii, and G. I. Nikishin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 140 [*Russ. Chem. Bull.*, 1993, **42**, 126 (Engl. Transl.)].
- 4. M. Katz, P. Riemenschneider, and H. Wendt, *Electrochim.* Acta, 1972, 17, 1595.
- 5. V. Plzak, H. Schneider, and H. Wendt, Ber. Bunsen-Gesellschaft Phys. Chem., 1974, 78, 1373.
- 6. R. Engels and H. J. Schäfer, Liebigs Ann. Chem., 1977, 204.
- 7. K. Sasaki and S. Nagaura, Bull. Chem. Soc. Jpn., 1965, 38, 649.
- 8. T. Inoue and S. Tsutsumi, Bull. Chem. Soc. Jpn., 1965, 38, 661.
- M. Kojima, H. Sakuragi, and K. Takamaru, Chem. Lett., 1981, 1707.
- 10. A. Bard, A. Ledwith, and H. J. Shine, Adv. Phys. Chem., 1976, 13, 155.
- 11. E. Baciocchi, Acta Chem. Scand., 1990, 44, 645.
- M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and D. Bartoli, *Tetrahedron*, 1988, 44, 2273.
- 13. S. Rozen, E. Mishani, and M. Kol, J. Am. Chem. Soc., 1992, 114, 7643.

Received April 6, 1994