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Electrosynthesis of arylalkanoic acids by oxidation of the corresponding arylalkanols at the Ni anode in aqueous alkali

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The electrochemical synthesis of a series of aryl(aryloxy)alkanoic acids was carried out by the electrocatalytic oxidation of the corresponding alcohols with the general formula RCH_2CH_2OH (R = Ar, CH_2Ph, OPh) in an undivided cell at the NiOOH electrode in aqueous alkali. The efficiency of the process depends on the structure of the starting alcohols, particularly, on the donor-acceptor properties of the substituent R. These properties determine the possibility of the primarily formed RCH_2COO^- anion to be oxidized forming by-products. The yield of the target acids upon the oxidation of 2-(2-hydroxyethyl)pyridine, 2-phenylethanol, 3-phenylpronan-1-ol, and 2-phenoxyethanol was 15, 53, 75, and 93%, respectively, based on the reacted alcohol.

Key words: electrocatalytic oxidation, nickelhydroxide anode, alcohols, arylacetic acids, carboxylic acids, aromatic compounds.

Interest in search for convenient methods of production of aryl-containing carboxylic acids is caused by their wide use in syntheses of drugs[1,2] and fragrances.[3] A rational approach seems to be the chemical oxidation of comparatively available respective aryl-substituted alcohols, which is accompanied, however, by "burning-out" of the aliphatic fragment[4] to form considerable amounts of benzoic acid.

We have earlier[5] developed successfully the method for synthesis of tetrazolylacetic acid by the electrooxidation (EO) of 1-(2-hydroxyethyl)tetrazole in an undivided cell at the Ni anode in aqueous alkali. This process results in the formation of NiOOH, being an efficient self-regenerating oxidant, on the anode surface. It could be expected that this method can also be used for the synthesis of arylacetic and arylpropionic acids. However, published information on the synthesis of phenylacetic acid by the electrooxidation of 2-phenylethanol at the NiOOH anode is rather contradictory. According to the published data,[6] the EO of this alcohol at the NiOOH anode in aqueous Bu^tOH afforded phenylacetic acid in high (66%) yield. In another paper it was reported[7] that in an alkaline medium at the NiOOH anode this acid was readily oxidized to benzoic acid in 80% yield. This stimulated us to study specially the EO of arylalkanols containing two and more CH_2 groups in the side chain at the NiOOH anode.

Results and Discussion

The earlier[6] studied 2-phenylethanol, which is well soluble in aqueous NaOH, was chosen as the first object of investigation. Even the first experiments on its EO under these conditions showed the presence of phenylacetic acid in the electrolysis products (Table 1, entry *1*). At the same time, the yield of phenylacetic acid (~18% based on the loaded alcohol) and the conversion of the initial 2-phenylethanol (31%) were low. The process simultaneously afforded noticeable amounts of benzoic acid (11% yield). The major steps of this process are presented in Scheme 1.

The study of the effect of various factors on this process shows that the temperature rise to 50 °C noticeably activates the process, increasing the conversion to 2-phenylethanol to 64%, and the yields of phenylacetic and benzoic acids increase to 34 and 19%, respectively (see Table 1, entries *1* and *2*). With an increase in NaOH concentration from 1 to 1.5 mol L^{-1} (see Table 1, entries *2* and *3*), the yield of phenylacetic acid decreases (by ~7%) and the yield of benzoic acid somewhat increases (by ~3%); lowering of NaOH concentration to 0.1 mol L^{-1} decreases both the conversion of the initial alcohol (by ~5%) and the yields of phenylacetic (by ~9%) and benzoic (by ~3%) acids (see Table 1, entries *2* and *4*—*6*).

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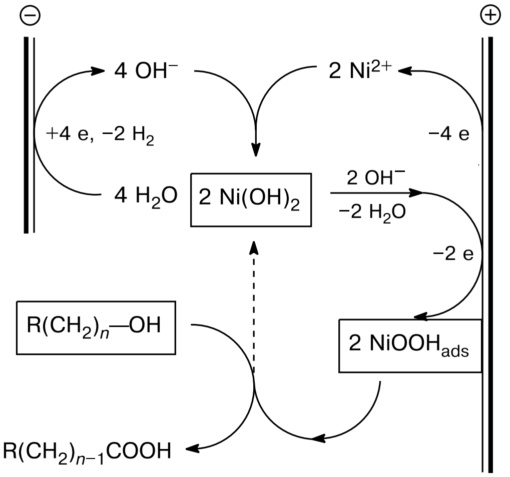
Table 1. Influence of the experimental conditions on the yield of phenylacetic (PAA) and benzoic (BA) acids upon the anodic oxidation of 2-phenylethanol (PE) in an aqueous solution of NaOH [a]

Entry	Concentration/mol L^{-1}		T/°C	J_a /mA cm^{-2}	Conversion of PE (%)	Q_{exp}/Q_{theor}	Molar ratio PAA : BA	Yield[b] (%)	
	PE	NaOH						PAA	BA
1	0.05	1.0	20	6	31	1.0	1 : 0.6	18 (58)	11
2	0.05	1.0	50	6	64	1.0	1 : 0.6	34 (54)	19
3	0.05	1.5	50	6	66	1.0	1 : 0.8	27 (41)	22
4	0.05	0.8	50	6	65	1.0	1 : 0.6	31 (48)	19
5	0.05	0.5	50	6	65	1.0	1 : 0.7	31 (47)	22
6	0.05	0.1	50	6	61	1.0	1 : 0.6	25 (41)	14
7	0.05	1.0	50	16	60	1.0	1 : 0.9	29 (48)	24
8	0.05	1.0	50	3	65	1.0	1 : 0.7	30 (47)	21
9	0.05	1.0	50	6	100	2.0	1 : 1.3	38 (38)	49

[a] Conditions: Ni anode, Ti cathode, $Q_{theor} = 4\,F$ (mole of PE)$^{-1}$.

[b] Calculated from the data of ^1H NMR spectroscopy for the isolated mixture of the electrolysis products; the yield based on reacted 2-phenylethanol is given in parentheses.

Scheme 1



The dependence of the yield of phenylacetic acid in the process considered on the current density passes through a maximum in which the yield reaches 34% (based on the loaded alcohol at J_a = 6 mA cm^{-2} (see Table 1, entries *2*, *7*, and *8*). An increase or decrease in the current density decreases the yield of the target product (by 4—6%) and results in some increase (by 1—5%) in the yield of benzoic acid. An attempt to increase the yield of phenylacetic acid due to an increase in the conversion of 2-phenylethanol with a double increase in the electric charge passed was unsuccessful. Although the conversion of 2-phenylethanol reached 100% (see Table 1, entries *2* and *9*), the yield of phenylacetic acid increased only by 4%. The yield of benzoic acid, by contrast, increased by more than two times, being 49%. Note that, as a whole, the yield of benzoic acid was, as a rule, rather high and the $[PhCH_2CO_2H] : [PhCO_2H]$ ratio in the electrolysis products ranged from 1 : 0.6 to 1 : 1.1, depending on the experimental conditions.

The presence of benzoic acid in the final reaction mixture is caused, most probably, by the further oxidation of the phenylacetic acid anion as the primary electrolysis product. For instance, this can explain the results of the above described experiment when an increase in the electric charge passed (see Table 1, entries *2* and *9*) increased the yield of benzoic acid. We believe that the further EO of the anion is caused by the high reactivity of its methylene group that is able to intramolecular proton abstraction to form the corresponding C-anion. This carbanion should be oxidized substantially more easily and accompanied by "burning-out" of the C atom removed as CO_2. The latter is transformed into the carbonate dianion in an alkaline medium (Scheme 2).

Scheme 2

$$PhCH_2COO^- \rightleftharpoons Ph\bar{C}HCOOH \qquad (1)$$

$$Ph\bar{C}HCOOH + 6\,NiOOH + 2\,OH^- + H_2O \longrightarrow$$

$$\longrightarrow PhCOO^- + CO_3^{2-} + 6\,Ni(OH)_2 \qquad (2)$$

It is quite obvious that equilibrium (1) is substantially shifted to the left. Nevertheless, the high ability of the C-anion to be oxidized, along with complete irreversibility of step (2), can result in the formation of noticeable amounts of benzoic acid during electrolysis.

If the proposed mechanism (see Scheme 2) is valid, the yield of the products in step (2) should depend on the easiness of the step, which in turn is predetermined by the withdrawing properties of the aromatic substituent. This forced us to study the regularities of the EO of

Table 2. Dependence of the yield of aryl-containing alkanoic and benzoic acids (AAA and BA, respectively) on the structure of aryl-containing alkanols ($C = 0.05$ mol L^{-1}) upon anodic oxidation in a 0.3 *M* solution of KOH in 50% aqueous Bu^tOH [a]

Entry	Starting alcohol	Q_{exp}/Q_{theor}	Conversion of alcohol (%)	Acids formed	Yield of acid[b] (%)	Molar ratio AAA : BA
1	$PhCH_2CH_2OH$	1	55	$PhCH_2COOH$	29 (53)	1 : 0.5
				PhCOOH	14 (25)	
2	$2,4,6\text{-}Me_3C_6H_2CH_2CH_2OH$	1	16	$2,4,6\text{-}Me_3C_6H_2CH_2COOH$	10 (61)	1 : 0.1
				$C_6H_2Me_3COOH$	1 (9)	
3	$PhOCH_2CH_2OH$	1	58	$PhOCH_2COOH$	54 (93)	—
4[c]	$2\text{-}C_5H_4NCH_2CH_2OH$	1	76	$2\text{-}C_5H_4NCH_2COOH$	12 (15)	1 : 5.2
				$2\text{-}C_5H_4NCOOH$	60 (79)	
5	$PhCH_2CH_2CH_2OH$	1	45	$PhCH_2CH_2COOH$	26 (75)	1 : 0.1
				$PhCH_2COOH$	1 (2)	
				PhCOOH	3 (8)	
6	$PhCH_2CH_2CH_2OH$	2	99	$PhCH_2CH_2COOH$	92 (94)	—
				PhCOOH	3 (3)	

[a] Conditions: Ni anode, Ti cathode, $J_a = 2.4$ mA cm^{-2}, $T = 50$ °C, $Q_{theor} = 4F$ per mole of starting alcohol.

[b] Calculated by the data of ^1H NMR spectroscopy for the isolated mixture of the electrolysis products; the yields based on the reacted alcohol are given in parentheses.

[c] Electrolysis was carried out in a 1 *M* aqueous solution of NaOH.

2-phenylethanol, 2-(2,4,6-trimethylphenyl)ethanol, 2-phenoxyethanol, 3-phenylpropan-1-ol, and 2-(2-hydroxyethyl)pyridine, representing a series of aryl-containing alkanols with the common formula RCH_2CH_2OH and different donor-acceptor properties of the substituents (Table 2).

Unlike 2-phenylethanol (R = Ph), the phenyl ring of 2-(2,4,6-trimethylphenyl)ethanol ($R = 2,4,6\text{-}Me_3C_6H_2$) contains three Me substituents that decrease the withdrawing properties of the ring and, as a consequence, the proton-donor properties of the methylene group, which, as we expected, should affect the character of the EO of 2,4,6-trimethylphenylethanol.

Since this compound is poorly soluble in aqueous NaOH, its EO was carried out in 50% aqueous Bu^tOH containing 0.3 *M* KOH (see Table 2, entry *2*). Under similar conditions (to provide a possibility of comparison of the experimental results), we also carried out the EO of 2-phenylethanol (see Table 2, entry *1*). From comparison of the data of entries *1* and *2* it follows that the EO of 2-(2,4,6-trimethylphenyl)ethanol affords the corresponding benzoic acid in an amount of fivefold smaller than that for the EO of 2-phenylethanol (the AAA : BA ratio in the electrolysis products varies from 1 : 0.5 to 1 : 0.1). These results completely confirmed our expectations.

The phenoxyl substituent in the case of 2-phenoxyethanol possesses much higher electron-donating properties. In fact, the EO of this compound under similar conditions (see Table 2, entry *3*) results in almost 100% formation of phenoxyacetic acid (93% yield based on the reacted alcohol). This acid cannot be oxidized further (see Scheme 2), because its methylene group has a very low acidity.

Finally, the data on the EO of 3-phenylpropan-1-ol ($R = PhCH_2$) are in complete accord with the developed theory. The benzyl substituent, unlike phenyl, has virtually no withdrawing properties, which determines differences in the data on the EO of 2-phenylethanol and 3-phenylpropan-1-ol (see Table 2, entries *1* and *5*). The yield of 3-phenylpropionic acid (entry *5*) was 75% (based on the reacted alcohol), and the yield of the products of its further oxidation, *viz*., phenylacetic and benzoic acids (with "burning-out" of one and two C atoms, respectively), did not exceed 3 and 8%, respectively.

At the same time, the conversion of the initial alcohol in this experiment (when the theoretical electric charge was passed) was low, being only 45%. To enhance the conversion, we doubled the electric charge. In this case, the conversion of 3-phenylpropan-1-ol (see Table 2, entry *6*) reached 99%, the yield of 3-phenylpropionic acid became close to quantitative (92%), and the yield of benzoic acid did not exceed 3%.

2-(2-Hydroxyethyl)pyridine was chosen as a substrate, because its substituent possesses higher electron-withdrawing properties than phenyl. The yield of (2-pyridyl)acetic acid upon the EO of this alcohol (see Table 2, entry *4*) was low (15% based on the reacted alcohol), whereas the major product was 2-pyridinecarboxylic acid (79% yield based on the reacted alcohol). According to the above data, the higher withdrawing properties of the pyridyl substituent favor the formation of the C-anion (see Scheme 2, reaction (1)) and, hence, the further oxidative destruction of 2-pyridineacetic acid.

In the conclusion, we showed a principal possibility of preparative EO of primary aryl-substituted alkanols at the NiOOH electrode to the corresponding arylpropionic or arylacetic acids and revealed the factors determining the selectivity of the process. It is found that the yield of benzoic acid formed as the by-product depends on the electronic properties of the aryl substituent in a molecule of the initial alcohol.

Experimental

Experiments were carried out under constant current using a B-5-8 dc source and a temperature-controlled (with a U-1 thermostat) undivided cell with the Ni anode (S = 45 cm^2) and Ti cathode (S = 20 cm^2). The electric circuit included the coulometer designed at the Special Design Bureau of the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. The solution was magnetically stirred during electrolysis. Before the process, the Ni anode was activated according to an earlier described procedure[8]: the electrolysis of the solution containing 0.1 M $NiSO_4$, 0.1 M NaOAc, and 0.005 M NaOH was carried out at J_a = 1 mA cm^{-2} with periodical reverse of polarity of the electrodes. The latter is necessary to form a NiOOH-containing multilayer coating on the anode surface.

The initial 2-phenylethanol, 2-(2,4,6-trimethylphenyl)ethanol, 2-phenoxyethanol, 2-(2-hydroxyethyl)pyridine, and 3-phenylpropan-1-ol (Acros) were used without additional purification.

The acids obtained by the EO of the alcohols were identified by ^{1}H NMR spectroscopy by comparing with the spectra of authentic samples of benzoic, 2-pyridinecarboxylic, (2-pyridyl)acetic, and 3-phenylpropionic acids (Acros). Authentic samples of phenoxyacetic[9] and 2,4,6-trimethylbenzoic[10] acids were synthesized by known procedures. The spectra of phenylacetic[11] and 2,4,6-trimethylphenylacetic[12] acids described in the literature were used. ^{1}H NMR spectra were recorded on a Bruker AC-200 instrument in DMSO-d$_6$.

Electrooxidation of 2-phenylethanol in an aqueous solution of NaOH (see Table 1, entry *2*). *A.* A 1 M solution of NaOH (100 mL) and 2-phenylethanol (0.6 mL, 0.005 mol) were placed in the cell, and electrolysis was carried out at a current of 270 mA and 50 °C. After 4 F per mole of starting substance of electricity were passed (Q = 1930 C), the electrolysis was stopped, the reaction mixture was stirred for 0.5 h, and the unreacted alcohol was extracted with $CHCl_3$ (3×30 mL). The extract was dried over Na_2SO_4, and $CHCl_3$ was distilled off under reduced pressure. A yellow oil, being 2-phenylethanol (according to the data of ^{1}H NMR spectroscopy), was obtained (0.22 g). The aqueous solution was acidified with concentrated HCl (to pH 1) and extracted with $CHCl_3$ (2×30 mL). The organic extract was dried over Na_2SO_4, the solvent was distilled off, and a crystallizing oil was obtained (0.35 g), being a mixture (according to the data of ^{1}H NMR spectroscopy) of phenylacetic and benzoic acids. The molar ratio of phenylacetic and benzoic acids was determined as 1 : 0.5 from the integral intensities of signals of phenylacetic and benzoic acids with δ 7.25 (s, 5 H, H arom.) and 8.05—7.50 (m, 5 H, H atom.), respectively. Taking into account these data, the yields of phenylacetic and benzoic acids were 34 and 19%, respectively, and the conversion of 2-phenylethanol was 64%.

Electrooxidation of 2-(2,4,6-trimethylphenyl)ethanol. *B.* A 50% aqueous solution of Bu^{t}OH (100 mL), KOH (1.68 g, 0.03 mol), and 2-(2,4,6-trimethylphenyl)ethanol (0.83 g, 0.005 mol) were placed in the cell, and electrolysis was carried out at a current of 108 mA and 50 °C. After 4 F mol^{-1} electricity were passed, Bu^{t}OH was salted out from the reaction solution by the addition of solid NaCl followed by the separation of the aqueous and organic phases. Under reduced pressure Bu^{t}OH was distilled off from the organic fraction. The residue obtained after distillation (unreacted starting alcohol with an admixture of NaCl) was mixed with water (5 mL), and the mixture was treated with $CHCl_3$ (2×10 mL). The organic layer was dried over Na_2SO_4, and 2-(2,4,6-trimethylphenyl)ethanol (0.67 g) was obtained after the solvent was distilled off (the substance was identified by ^{1}H NMR spectroscopy). Aqueous fractions (after the alcohol was isolated) were mixed together, acidified with concentrated HC1 (to pH 1), and extracted with $CHCl_3$ (3×25 mL). The extract was dried over Na_2SO_4, the solvent was distilled off, and a white powder (0.12 g) was obtained. According to the data of ^{1}H NMR spectroscopy, the powder was a mixture of 2,4,6-trimethylphenylacetic acid, 2,4,6-trimethylbenzoic acid, and 2-(2,4,6-trimethylphenyl)ethanol. The molar ratio of these components in the reaction mixture was determined as 1 : 0.1 : 0.3 from the integral intensities of signals of 2,4,6-trimethylphenylacetic acid, 2,4,6-trimethylbenzoic acid, and 2-(2,4,6-trimethylphenyl)ethanol with δ 6.75 (s, 2 H, H arom.), 6.80 (s, 2 H, H arom.), and 6.70 (s, 2 H, H arom.), respectively. Taking into account these data, the yield of 2,4,6-trimethylphenylacetic and 2,4,6-trimethylbenzoic acids was 10 and 1%, respectively, and the conversion of 2-(2,4,6-trimethylphenyl)ethanol was 16%.

Electrooxidation of 2-phenoxyethanol. *C.* A 50% aqueous solution of Bu^{t}OH (100 mL), KOH (1.68 g, 0.03 mol), and 2-phenoxyethanol (0.69 g, 0.005 mol) were placed in the cell. Electrolysis in an alkaline aqueous-alcohol medium was carried out according to method ***B***. After the completion of the electrolysis and isolation of the products (see above), unreacted 2-phenoxyethanol (0.27 g, identified by ^{1}H NMR spectroscopy, 58% conversion) and a solid substance, being (according to the data of ^{1}H NMR spectroscopy) 2-phenoxyacetic acid containing ~5% 2-phenoxyethanol (0.43 g), were obtained. To purify the acid, the latter was transformed into the salt by the treatment with a solution of NaOH (0.2 g, 0.005 mol) in water (5 mL), and 2-phenoxyethanol was extracted with $CHCl_3$ (2×3 mL). The organic extract was rejected, and the aqueous solution was acidified with concentrated HCl (to pH 1) and extracted with $CHC1_3$ (2×3 mL). After the solvent was distilled off, 2-phenoxyacetic acid was obtained (0.33 g, 43%), m.p. 100 °C (*cf.* Ref. 9: m.p. 99 °C). ^{1}H NMR, δ: 6.90—7.25 (m, 5 H, H arom.); 4.55 (s, 2 H, CH_2).

Electrooxidation of 2-(2-hydroxyethyl)pyridine. A solution of NaOH (100 mL) and 2-(2-hydroxyethyl)pyridine (0.57 mL, 0.005 mol) were placed in the cell. Electrolysis was carried out according to method ***A***. After the completion of the electrolysis, the unreacted alcohol was removed by extraction with $CHC1_3$ (3×35 mL). The extract was dried over Na_2SO_4, the solvent was distilled off, and an oil (0.15 g) was obtained, which was unreacted 2-(2-hydroxyethyl)pyridine identified by ^{1}H NMR spectroscopy. The aqueous phase was acidified with concentrated HCl (to pH 1), water was distilled off under reduced pressure, and the solid residue was treated with acetone (1×15 mL) and EtOH (3×25 mL) and filtered. The filtrates were mixed, the solvents were distilled off, and an oil (0.75 g), which was (according to the data of ^{1}H NMR spectroscopy) a mixture of 2-pyridinecarboxylic acid, (2-pyridyl)acetic acid, and

2-(2-hydroxyethyl)pyridine, was obtained. The molar ratio of 2-pyridinecarboxylic acid, (2-pyridyl)acetic acid, and 2-(2-hydroxyethyl)pyridine was determined as 5.2 : 1 : 1 from the integral intensities of the characteristic signals of (2-pyridyl)acetic acid with δ 3.29 (s, 2 H, CH_2), 2-(2-hydroxyethyl)pyridine with δ 2.80 (s, 2 H, CH_2), and the total signals of the pyridyl fragment of these components with δ 7.80—8.85 (m, 4 H, H arom.) Taking into account these data, the yield of (2-pyridyl)acetic and 2-pyridinecarboxylic acids was 12 and 60%, respectively, and the conversion of 2-(2-hydroxyethyl)pyridine was 76%.

Electrooxidation of 3-phenylpropan-1-ol (see Table 2, entry *6*). A 50% aqueous solution of Bu^tOH (100 mL), KOH (1.68 g, 0.03 mol), and 3-phenylpropan-1-ol (0.7 mL, 0.005 mol) were placed in the cell, and electrolysis was carried out according to method ***B***, passing 8 F mol^{-1} electricity (totally 3860 C). After the completion of the electrolysis and isolation of the products (see above), 3-phenylpropan-1-ol (0.008 g, identified by ^{1}H NMR spectroscopy, conversion of alcohol 99%) and a solid substance (0.7 g) were obtained. According to the data of ^{1}H NMR spectroscopy, the solid was 3-phenylpropionic acid containing ~3% benzoic acid as an admixture. After recrystallization from water, pure 3-phenylpropionic acid was obtained (0.48 g, 64%), m.p. 48—49 °C (*cf.* Ref. 13: m.p. 48 °C). ^{1}H NMR, δ: 7.20 (m, 5 H, H arom.); 2.55, 2.90 (both t, 2 H each, CH_2—CH_2, J = 7.4 Hz).

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