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Electrosynthesis of adipic acid by undivided cell electrolysis

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A preparative method for synthesis of adipic acid in 47% yield was developed. The method is based on cyclohexanol oxidation in an undivided cell on the NiOOH electrode in aqueous alkali. A possibility of the step-by-step process was studied: oxidation of cyclohexanol to cyclohexanone (75% yield) and subsequent oxidation of cyclohexanone to adipic acid (52% yield). The electrosynthesis of adipic acid is accompanied by the formation of minor amounts (up to 10%) of glutaric and succinic acids.

Key words: electrosynthesis, adipic acid, nickel/nickel hydroxide anode, cyclohexanol, cyclohexanone.

Adipic acid is widely used and, hence, researchers are interested in the development of convenient methods of its synthesis.[1] Our emphasis is on a possibility of electrosynthesis of adipic acid by the electrooxidation of cyclohexanol in an aqueous alkaline medium on the nickel anode in an undivided cell, because NiOOH, which is formed on the Ni anode surface and self-regenerated during electrolysis, is a sufficiently efficient oxidant. We successfully used this approach earlier[2] for the oxidation of 1-(2-hydroxyethyl)tetrazole to obtain tetrazolylacetic acid, which is an intermediate in the synthesis of antibiotic Cefazolin. Note that the fact of preparation of cyclohexanone (CHN) by cyclohexanol (CHL) oxidation on the NiOOH electrode has been described previously.[3] However, data on the specific features of this process are lacking. A possibility to synthesize adipic acid (AA) by cyclohexanol electrooxidation was not studied. One of the expected difficulties is that the oxidation of the secondary hydroxy group proceeds through the intermediate formation of ketone, which is poorly oxidized and prone to self-condensation.

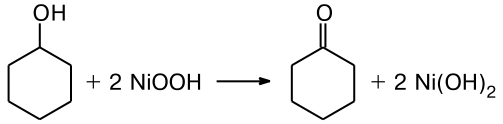
Taking into account these circumstances, we performed this study in two stages. At the first stage, we studied the factors determining the efficiency of cyclohexanol oxidation to cyclohexanone on the NiOOH electrode. At the second stage, we examined a possibility of cyclohexanone oxidation to adipic acid and revealed the regularities of this process. We assumed that the successful occurrence of these stages makes it possible to perform the one-step transformation of cyclohexanol into adipic acid.

Results and Discussion

The expected mechanism of cyclohexanol electrooxidation in an undivided cell on the NiOOH anode in an aqueous solution of NaOH can be described by Scheme 1.

Scheme 1

Anode: $2\ \mathrm{Ni(OH)_2} + 2\ \mathrm{OH^-} - 2\mathrm{e} \longrightarrow 2\ \mathrm{NiOOH} + 2\ \mathrm{H_2O}$



Cathode: $2\ \mathrm{H_2O} + 2\mathrm{e} \longrightarrow 2\ \mathrm{OH^-} + \mathrm{H_2}$

The study of the regularities of this process revealed that the yield of cyclohexanone depended slightly on the initial alcohol concentration* (C_0^{CHL}) (Table 1, entries *1—3*), reaching the maximum value (75.6%) at $C_0^{\mathrm{CHL}} = 0.15$ mol L^{-1}. The plot of the cyclohexanone yield *vs.* current density (j) passes through a maximum (see Table 1, *cf.* entries *1*, *4*, and *5*) achieving 75.6% at $j = 6$ mA cm^{-2}. It is most likely that an increase in j is

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* The solubility of cyclohexanol depends on the alkali concentration. However, the alcohol loaded was completely dissolved during electrolysis.

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Table 1. Influence of the experimental conditions on the yields of cyclohexanone (CHN) and adipic acid (AA) in the electrooxidation of cyclohexanol (CHL) in an undivided cell in an aqueous solution of NaOH

Entry	CHL	NaOH	T/°C	j/mA cm^{-2}	Yield[a] (%) CHN[b] (AA)	
	/mol L^{-1}				I	II
1	0.10	1.00	30	6	70.3	70.3
2	0.15	1.00	30	6	75.6	75.6
3	0.30	1.00	30	6	68.6	68.6
4	0.15	1.00	30	3	61.4	61.4
5	0.15	1.00	30	16	64.1	64.1
6	0.15	0.30	30	6	50.1	50.1
7	0.15	0.50	30	6	55.1	55.1
8	0.15	0.80	30	6	67.1	67.1
9	0.15	1.20	30	6	65.4	65.4
10	0.15	1.00	10	6	74.4	74.4
11	0.15	1.00	50	6	32.5 (11.4)	32.5 (41.8)[c]
12[d]	0.15	1.00	10	6	70.3 (9.4)	44.6 (23.9)[c]

Note. NiOOH is anode, Ti is cathode, $Q_{\text{theor}} = 2\,F$ per 1 mole of cyclohexanol.

[a] I is the substance yield, and II is the current efficiency.

[b] Calculated to the starting cyclohexanol (determined as 2,4-dinitrophenylhydrazone).

[c] Calculated to the eight-electron oxidation of cyclohexanol.

[d] $Q = 1.5\,Q_{\text{theor}}$.

accompanied by an increase in the contribution of the side process on the anode

$$4\,OH^- - 4\,e \rightarrow 2\,H_2O + O_2.$$

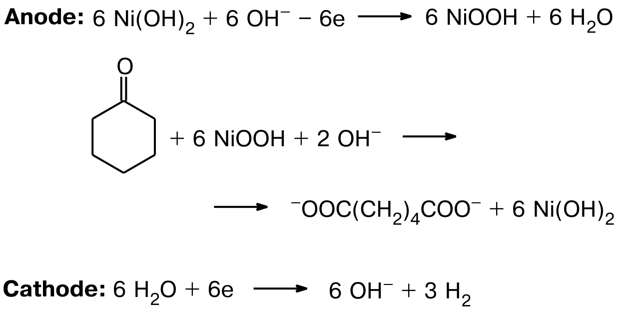
An increase in the alkali concentration in a range of 0.3—1.0 mol L^{-1} also increases the yield of cyclohexanone (see Table 1, entries *2*, *6*—*8*). However, at the higher alkali concentration (C^{NaOH} = 1.2 mol L^{-1}, entry *9*), the yield of ketone decreases by ~10%. A temperature change in the 10—30 °C range has virtually no effect on the cyclohexanone yield (entries *2* and *10*), and at 50 °C the formation of adipic acid was detected in the final reaction mixture (entry *11*). The temperature increase evidently favors the oxidation of cyclohexanone itself. This is indicated by the fact that acid formation is accompanied by a considerable decrease in the yield of cyclohexanone when the amount of passed electricity is equal for all entries (2 *F* per 1 mole of starting cyclohexanol (see Table 1, *cf.* entries *2* and *11*).

Thus, the variation of electrolysis conditions made it possible to increase the yield of cyclohexanone, although not higher than 75%. It is most probably that this is caused by the side process of anodic oxidation of hydroxide ions. An attempt to suppress this process by an increase in the electrolysis duration (entry *12*) was unsuccessful: the yield of cyclohexanone even decreased slightly, and adipic acid was formed simultaneously. Evidently, cyclohexanone accumulation in a solution and the temperature increase favor its further oxidation.

Thus, the first stage of studies made it possible to optimize the conditions (C_0^{CHL} = 0.15, C^{NaOH} = 1.0 mol L^{-1}, T = 10—30 °C, j = 6 mA cm^{-2}) providing a high yield (74.5—75.5%) of the target product. Simultaneously we established a principal possibility of the one-step oxidation of cyclohexanol to adipic acid.

The next stage is related to revealing a possibility of the electrooxidation of cyclohexanone to adipic acid on the NiOOH electrode. In general, the expected transformations can be described by Scheme 2.

Scheme 2



The results of the studies are presented in Table 2. It is known[4] that NaOH and KOH induce the croton condensation of cyclohexanone. Therefore, in the first experiments (see Table 2, entries *1* and *2*) solutions of K_2CO_3 were used instead of NaOH solutions. However, the yield of adipic acid was very low (2—3%), and the conversion of cyclohexanone did not exceed 7%. It can be assumed that the amount of the enolic form (this form is most probably oxidized) is low in a low-basicity medium. Therefore, further experiments were carried out in a solution of NaOH. This increased the yield of adipic acid from 3 to 19%, and the ketone conversion was increased from 7 to 57%. The variation of the experimental conditions showed that the plot of the acid yield *vs.* increase in the NaOH concentration passes through a maximum at C^{NaOH} = 1.0 mol L^{-1} (see Table 2, *cf.*, entries *3*—*8*). The optimum j value for ketone oxidation is the same as that for alcohol oxidation and is equal to 6 mA cm^{-2} (see Table 2, *cf.* entries *3*, *8*, and *9*). At the same time, it is seen from the data in Table 2 that only 41% reacted ketone are transformed into the acid, although the cyclohexanone conversion reaches 80%.

The further optimization of the process showed that adipic acid formation was favored by a decrease in the temperature and an increase in C_0^{CHN}. For instance, the yield of acid per reacted ketone at 10 °C increased to

Table 2. Influence of the experimental conditions on the yields of adipic (AA), glutaric (GA), and succinic (SA) acids during cyclohexanone electrooxidation in an undivided cell in an aqueous solution of NaOH

Entry	CHN	NaOH	T/°C	Conversion of CHN (%)	Q/Q_{theor}	j/ mA cm^{-2}	Yield[a] (%)			
	mol L^{-1}						AA		GA	SA
							I	II	I	
1[b]	0.15	0.30	30	4		6	2.3	57.5	—	—
2[b]	0.15	0.3	30	7	1	6	3.0	42.8	—	—
3	0.15	0.3	30	56.9	1	6	19.3	33.9	7.1	3.1
4	0.15	0.4	30	63.3	1	6	22.0	34.7	7.5	3.2
5	0.15	0.6	30	70.3	1	6	22.3	31.7	8.1	3.5
6	0.15	1.0	30	80.1	1	6	33.1	41.2	7.8	3.3
7	0.15	1.2	30	87.1	1	6	30.1	34.5	12.6	5.5
8	0.15	1.0	30	72.7	1	3	23.8	32.7	8.2	3.7
9	0.15	1.0	30	27.6	1	16	16.5	37.9	2.8	1.2
10	0.15	1.0	50	95.0	1	6	28.7	30.2	15.3	7.1
11	0.15	1.0	10	27.9	1	6	12.6	45.3	4.1	0.8
12	0.21	1.0	10	34.5	1	6	18.5	53.7	5.9	1.1
13	0.30	1.0	10	37.3	1	6	21.4	57.4	6.9	1.2
14	0.15	1.0	10	42.3	1.5	6	21.6	51.1	6.0	1.7
15	0.15	1.0	10	58.8	2.3	6	28.4	48.3	8.5	2.5
16	0.15	1.0	10	70.2	4.0	6	36.7	52.3	9.3	3.7

Note. NiOOH is anode, Ti is cathode, $Q_{\text{theor}} = 2\ F$ per 1 mole of cyclohexanone.

[a] I is the yield with respect to the starting cyclohexanone (calculated from the ^{1}H NMR data of an isolated mixture of the electrolysis products), and II is the yield with respect to the reacted cyclohexanone.

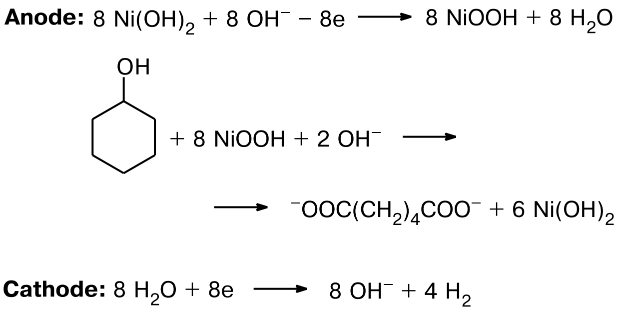
[b] K_2CO_3 was used instead of NaOH.

45.3% (*cf.* entries *6*, *10*, and *11*), whereas it increased by 12% with an increase in C_0^{CHN} (*cf.* entries *11—13*). Despite a satisfactory yield of acid (45%), the conversion of cyclohexanone remained rather low (~28%). This disadvantage was partially eliminated by an increase in the amount of passed electricity (see Table 2, *cf.* entries *11*, *14—16*). For instance, a fourfold (compared to the theoretical value) increase in Q (entry *16*) resulted in the 70% ketone conversion and simultaneously increased the acid yield to 52%. Thus, the result of the second stage of the studies is the optimization of the experimental conditions (C_0^{CHN} = 0.15—0.30 mol L^{-1}, C_{NaOH} = 1.0 mol L^{-1}, T = 10 °C, j = 6 mA cm^{-2} and $Q = 4\ Q_{\text{theor}}$), which provided a quite satisfactory yield ($\geq$52%) of adipic acid.

It is of interest that glutaric (substance yield 4—9%) and succinic (substance yield 0.8—3.7%) acids are formed in minor amounts along with adipic acid by the electrooxidation of cyclohexanone under the experimental conditions (see Table 2). It can be assumed that their formation is induced by the partial oxidative destruction of the cyclohexanone ring (oxidation of one or two carbon atoms to CO_2) at early steps of electrolysis, because adipic acid is not oxidized under the experimental conditions.

As a whole, the results considered above are a good prerequisite for the development of one-step transformation of cyclohexanol into adipic acid omitting the step of intermediate cyclohexanone formation. In the general form, the expected reactions can be described by Scheme 3.

Scheme 3



The acid yield increases during electrolysis with an increase in C_0^{CHL} (Table 3, entries *1—3*) but remains low (~21%) when the theoretical amount of electricity is passed. In addition, the solution after electrolysis contains a considerable amount of cyclohexanone due to its incomplete conversion to adipic acid. An increase in the amount of passed electricity increased the ketone conversion (see Table 3, entries *4—6*), and the yield of adipic acid increased substantially to be already 46.7%. In should be emphasized that the electrolysis of cyclohexanol (as

Table 3. Influence of the experimental conditions on the yields of cyclohexanone (CHN) and adipic acid (AA) and on the total yield of glutaric (GA) and succinic acids (SA) in the electrooxidation of cyclohexanol in a 0.1 *M* aqueous solution of NaOH

Entry	CHL /mol L^{-1}	Q/Q_{theor}	Yield (%)					
			CHN[a,b]		AA[a,c]		GA[c]	SA[c]
			I	II	I	II		
1	0.10	1.0	66.8	16.70	19.2	19.20	6.60	1.2
2	0.15	1.0	64.2	16.00	21.1	21.10	3.30	1.1
3	0.20	1.0	39.3	9.60	37.8	37.80	8.20	1.4
4	0.15	0.8	73.8	23.80	21.4	34.20	2.55	0.6
5	0.15	2.0	30.0	3.75	36.9	18.20	9.40	3.7
6	0.15	4.0	17.7	1.10	46.7	11.52	11.50	6.3

Note. NiOOH is anode, Ti is cathode, $Q_{\text{theor}} = 8$ *F* per 1 mole of cyclohexanol, $j_a = 6$ mA cm^{-2}, $T = 10$ °C.

[a] I is the substance yield, and II is the current efficiency.

[b] Per the starting cyclohexanol (determined as 2,4-dinitrophenylhydrazone).

[c] Per the starting cyclohexanol (calculated by the ^{1}H NMR data for an isolated mixture of the electrolysis products).

for cyclohexanone electrooxidation, see above) affords glutaric and succinic acids in minor amounts along with adipic acid (see Table 3).

It should be noted in conclusion that we showed a possibility of electrooxidation of ketones to carboxylic acids on the NiOOH electrode in an aqueous alkaline medium with a satisfactory yield using cyclohexanone as an example. This possibility was used for the development of a preparative method for synthesis of adipic acid by cyclohexanone electrooxidation under the experimental conditions.

Experimental

Electrolysis was carried out in an undivided cell with the Ni anode ($S = 124$ cm^2) and Ti cathode ($S = 40$ cm^2) equipped with a water jacket for temperature control. Electrolysis was carried out in an amperostatic regime using a B5-8 dc source. A coulometer designed at the Specialized Design Office of the Institute of Organic Chemistry of the RAS was connected into the electric circuit. The temperature was maintained by a U-1 thermostat. A magnetic stirrer was used to stir the reaction mixture during electrolysis. Before experiments, the Ni anode was activated using a known procedure[3] by the preliminary electrolysis in a solution containing 0.1 *M* $NiSO_4$, 0.1 *M* NaOAc, and 0.005 *M* NaOH at $j = 1$ mA cm^{-2} with a periodical reversal of electrode polarization. This procedure is necessary to form a multilayer NiOOH-containing coating on the Ni anode surface. A working solution was prepared using distilled water and a titrated solution of NaOH (pure grade).

To identify cyclohexanone and determine its yield, it was transformed into 2,4-dinitrophenylhydrazone using a known procedure.[5] Acids formed (adipic, glutaric, and succinic) were identified by ^{1}H NMR spectroscopy (solvent DMSO-d_6) on a Bruker AC-200 instrument using comparison with spectra of authentic samples.

Electrooxidation of cyclohexanol to cyclohexanone (general procedure exemplified by entry *12*, Table 1). An electrolytic cell was filled with a 1 *M* aqueous solution of NaOH (200 mL) and cyclohexanol (3.1 mL, 0.03 mol), and electrolysis was carried out at a current of 0.744 A and 10 °C. After 3 *F* electricity was passed per 1 mole of cyclohexanol, electrolysis was stopped. The reaction mixture was stirred for 0.5 h and neutralized with concentrated HCl (to pH 6—7). Then an aliquot of this solution was taken to identify cyclohexanone and to determine its yield, which was 70.3% (substance yield) and 44.6% (current efficiency). Concentrated HCl was added to the remaining reaction mixture (to pH 1—2), and water was distilled off under a reduced pressure. The dry salt residue was extracted with acetone (4×25 mL). After acetone was distilled off, adipic acid (0.41 g) was obtained and identified by the ^{1}H NMR spectra (comparing with that of the authentic sample) and m.p. 152 °C (Ref. 6: 153 °C). The substance yield of adipic acid was 9.4% and its current efficiency was 23.9%.

Electrooxidation of cyclohexanone to adipic acid (general procedure exemplified by entry *16*, Table 2). A cell was filled with a 1 *M* aqueous solution of NaOH (200 mL) and cyclohexanone (3.1 mL, 0.03 mol), and electrolysis was carried out at a current of 0.744 A and 10 °C. After 24 *F* electricity was passed per 1 mole of cyclohexanone, electrolysis was stopped, and the cyclohexanone conversion was determined (as described above), which was 70.2%. After the reaction mixture was treated as described above, a powder (2.11 g) was isolated, which was, according to the data of ^{1}H NMR spectroscopy, a mixture of adipic, glutaric, and succinic acids. The molar ratio of the products equal to 9.9 : 2.5 : 1 was determined from integrated intensities of the signals (adipic acid: δ 1.50 (m, 4 H, CH_2), glutaric acid: 1.70—1.88 (m, 2 H), and succinic acid: 2.40 (4 H, CH_2)). The yields of these acids (per loaded cyclohexanone) were 36.7, 9.3, and 3.7%, respectively. To isolate adipic acid from the mixture, the powder (2.11 g) was rinsed with water (3×5 mL) and dried. The amount of adipic acid obtained was 0.86 g (60% of the mixture content, according to the data of the ^{1}H NMR spectra), m.p. 153—154 °C (Ref. 6: 153 °C).

Electrooxidation of cyclohexanol to adipic acid (general procedure exemplified by entry *6*, Table 3). A cell was filled with a 1 *M* aqueous solution of NaOH (200 mL) and cyclohexanol (3.1 mL, 0.03 mol). Electrolysis was carried out as described above, passing 32 *F* electricity per 1 mole of cyclohexanol. After the end of electrolysis and isolation of the products as described above, cyclohexanone and adipic, glutaric, and succinic acids were obtained with substance yields of 17.7 and 46.7, 11.5, and 6.3%, respectively.

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