ON THE ROLE OF THE STATE OF THE SURFACE OF THE CATHODE IN THE ELECTROREDUCTION OF AROMATIC NITRO COMPOUNDS

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The course of the electroreduction process of organic ompounds depends to a large extent on the nature of the cathode material. One of the basic causes of the existence of this dependence is the hydrogen overvoltage. It is customary to assume that the greater the hydrogen overvoltage at the cathode, the higher its reducing properties, i.e., the more profoundly and intensively electroreduction process proceeds [1]. If the hydrogen overvoltage at the given cathode is small, then it is difficult to count on a high effectiveness of the reduction of organic depolarizers (in particular, if it belongs to the weak class), since at strong polarization the cathode begins to evolve hydrogen. Thus, during the reduction of nitrobenzene in acid medium on cathodes of zinc or lead the formation of aniline will proceed. By the use as cathode of platinum, the product of the incomplete reduction of nitrobenzene – phenylhydroxylamine [2] is formed. This is explained by the fact that at a platinum cathode the reduction potential of phenylhydroxylamine to aniline is more negative than the potential for the evolution of hydrogen; consequently in place of the reduction of phenylhydroxylamine the evolution of hydrogen will occur.

The direction and intensity of the process of electroreduction are determined not only by the nature of the cathode material.

Preliminary treatment of the cathode, consisting in placing on its surface a spongy (and in a number of cases dense galvanic) deposit of metals, pickling, mechanical treatment, etc. exerted a very substantial influence on the direction of the electroreduction process in a number of cases. Such preliminary treatment makes it possible to successfully reduce various organic compounds on metals with low hydrogen overvoltages. Tafel further noted the fact that on spongy lead the electroreduction proceeds with greater effectiveness than on smooth lead and proposed a method of special treatment of the surface of a lead cathode before the synthesis [3].

Lebedev and his coworkers, in the course of a study of the electrohydrogenation of vinylacetylene, established that the process proceeds with excellent yields only on copper or brass cathodes covered with platinum black [4]. On smooth platinum the process proceeds poorly. There are indications concerning the role of preparing the surface of the cathode in the electrohydrogenation of acetylenic alcohols in the works of Favorskaya [5] and Lebedeva [6].

The preliminary placing of various metals on the surface of the cathode by the galvanic method which considerably increases its reduction capacity has a substantial significance in a number of cases. Thus, in the reduction of methylethylketone Izgaryshev and Aryamova successfully used a copper cathode having the form of a spiral, covered with electrolytic lead [7].

Preliminary treatment of the cathode, which facilitates the increase in the effectiveness of the reduction of organic substances does not always lead to the simultaneous increase of hydrogen overvoltage on the cathode. On spongy metals, for example, the hydrogen overvoltage is lower than on smooth metals, while the effectiveness of the electroreduction in a number of cases is considerably greater. At the same time the lowering of the hydrogen overvoltage on the spongy cathodes sometimes reaches 0.4 V, in comparison with smooth cathodes [8]. There are cases in which on both cathodes on which the hydrogen overvoltage is great, the electroreduction proceeds with high effectiveness, while on other cathodes, also with great hydrogen overvoltage, the reduction process proceeds very poorly. This can be seen in the case of the electroreduction of 2-chloromethyl-4-nitrotoluene into o-4-xylidene, studied by Berezovsky and Varkov [9]. These authors detected that the reduction of 2-chloromethyl-4-nitrotoluene proceeds with high yields on cathodes made of zinc and lead. The yield of o-4-xylidene is considerably lowered by the use as cathode of mercury or copper, and is entirely unsatisfactory when the reduction is carried out on a cathode of tin.

Apparently, the fact of the absence of a known relation between the hydrogen overvoltage and the effectiveness of the cathode reduction, established for a large quantity of syntheses, argues in favor of the catalytic influence of the surface of the cathode on the electroreduction of a number of organic depolarizers. The fact that the surface of the metal can exert catalytic influence on the cathodic and anode processes is discussed in the work of Pecherskaya and Stender [10].

The object of our work was the study of the electroreduction process of o-,m- and p-nitrobenzoic acids into the corresponding aminobenzoic acids on various cathodes. It is necessary to make the reservation that we did not pursue the goal of establishing the dependence of the yields of aminobenzoic acids on the nature of the cathode. The present investigation should be considered as an attempt to find the relation between the state of the surface of each of the cathodes investigated and the yields of aminobenzoic acids at various temperatures, concentration of hydrochloric acid and current densities. A brief note on the work already carried out has been published previously by us [11].

EXPERIMENTAL

Apparatus and Method of Investigation. The reduction of nitrobenzoic acids was studied on cathodes of tin, lead, amalgamated zinc, copper and graphite. The cathodes consisted of perforated cylinders which were placed in a porous cylindrical diaphragm, which served as a cathode space. The anode was prepared from sheet lead. The nitrobenzoic acid was introduced into the cathode space in the form of a suspension in hydrochloric acid. 15% sulfuric acid served as the anolyte in all cases. The suspension of nitrobenzoic acid was stirred with a mechanical stirrer. To maintain the determined temperature the electrolyzer was placed in a thermostat supplied with a thermoregulator. The yields of aminobenzoic acids were determined by diazotization. The measurement of the melting points of the aminobenzoic acids evolved from the catholyte after completion of the electroreduction process proved to be in excellent agreement with the literature data.

The study of the influence of the state of the surface of the cathode on the yields of aminobenzoic acids was carried out at various temperatures, current densities, concentrations of hydrochloric acid and added quantities of $CuCl_2 \cdot 2H_2O$. The reproducibility of the results of experiments carried out under identical conditions was excellent (1-2%).

1. Study of the Influence of Temperature. The nitrobenzoic acids in quantities of 5 g were reduced at various temperatures (20-75°) on cathodes of tin, lead, amalgamated zinc, copper and graphite. 2.32 N hydrochloric acid served as electrolyte, the current density at the cathode amounted to 8 A per square decimeter. In the reduction of the nitrobenzoic acids on cathodes of copper and graphite, good results could be obtained only in the presence of 1-7 g of $CuCl_2 \cdot 2H_2O$. The introduction of this additive facilitated the increase in the yields of aminobenzoic acids according to substance, but lowered their yields according to current, since to eliminate the Cu^{++} ions from the solution an additional quantity of electricity was passed, which was taken into account in the calculation of the yield by current.

In Table 1 are set forth the yields of aminobenzoic acids by substance at various temperatures.

TABLE 1
Yields of Aminobenzoic Acids by Substance at Various Temperatures on Various Cathodes

Temp.	Yield of acids (in %)														
	o-Aminobenzoic					m-Aminobenzoic					p-Aminobenzoic				
	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C
20°	65.7	48.8	68.0	68.7	–	91.6	60.1	72.3	72.8	42.6	29.3	5.4	–	–	–
30	94.5	81.4	87.8	73.2	38.4	96.7	69.4	90.1	75.4	52.2	38.9	13.0	–	11.4	18.2
40	98.0	88.2	96.5	65.2	42.6	95.6	85.1	90.9	73.2	83.3	51.6	34.2	–	28.5	43.7
50	99.0	86.9	97.3	52.6	42.9	97.0	84.8	95.0	–	74.5	63.4	67.1	–	46.4	76.8
60	98.5	85.4	97.5	48.7	–	97.2	85.8	94.8	84.3	62.4	93.4	87.9	–	69.1	66.9
70	97.7	84.2	97.3	–	–	92.2	77.8	95.1	82.7	50.4	94.6	88.1	–	78.4	70.4
75	96.8	–	97.8	–	–	90.1	–	94.7	80.6	–	95.3	84.7	–	73.8	70.9

Observations on the course of the syntheses showed that in the first instants after switching on the current a precipitate of copper is formed on cathodes of copper and graphite. This was particularly noticeable on graphite. The source of the copper which settled out on the copper and graphite cathodes was the Cu^{++} ions introduced into the catholyte in the form of the chlorous salt. With the use as cathode material of tin a considerable portion of the nitrobenzoic acids was reduced chemically, apparently, due to the reaction $Sn^{++} \rightarrow Sn^{++++}$.

It was indicated in one of the works that the yields of p-aminobenzoic acid on cathodes of tin and lead reached 98% only in the presence of 3-5 g of $SnCl_2 \cdot 2H_2O$ per 5 g p-nitrobenzoic acid [12]. We showed that it is in general possible to avoid the use of stannous chloride but at the same time is necessary to increase the intensity of stirring the suspension of p-nitrobenzoic acid by 3–4 times.

Apparently in the work of the above mentioned authors the intensity of stirring was insufficient for regular

intake of p-nitrobenzoic acid at the cathode and its electrochemical reduction. The role of the introduced addition of $SnCl_2 \cdot 2H_2O$ probably consisted in the chemical reduction of that portion of the p-nitrobenzoic acid which, due to the insufficient effectiveness of the stirring, did not succeed in reaching the cathode. It is noteworthy that in all cases in which the cathode is formed of light sponge with a developed surface, the yields of aminobenzoic acids are increased, and, on the contrary, the formation of a dark precipitate on the surface of copper or graphite cathodes facilitates a marked reduction in the yields. The behavior of the lead cathode is very interesting. The study of the results of the synthesis on a lead cathode shows a considerable dependence of the yields of aminobenzoic acids on the temperature. This is probably associated with increased solubility of lead in hydrochloric acid with increased temperature. Since the unique source of the lead ions by the discharge of which the formation of sponge on the cathode proceeds, is the material of the cathode, it is understandable that at higher temperatures the sponge will have a maximal surface. The increase in the effectiveness of the reduction in this case cannot be ascribed to anything other than the spongy structure of the surface of the cathode. The participation of the Pb^{++} ions in the reduction reaction is excluded, since divalent lead does not have reducing properties. Attempts to reduce p-nitrobenzoic acid at a cathode of amalgamated zinc did not give positive results. This is explained by the fact that p-nitrobenzoic acid is poorly suspended in hydrochloric acid, while since upon dissociation of the amalgam there proceeds strong evolution of hydrogen, a foam is formed which is discharged from the electrolyzer and carries away particles of p-nitrobenzoic acid. The great losses of p-nitrobenzoic acid under these conditions distort the results and compelled us to withhold this isomer from reduction at a cathode of amalgamated zinc.

2. Study of the Influence of Additives. Additions of the salts of metals which facilitate the increased effectiveness of the electroreduction of organic substances, can be separated into 2 groups.

No particular doubts arise relative to the mechanism of action of polyvalent ions of the metals. Ions of the Ti^{+++}, Fe^{++}, Cr^{++}, V^{++++} type and others, introduced into the catholyte in the form of salts in which they have a lower valence, chemically reduce the organic substances and are thereby converted into the higher valence. At the cathode reduction of the ions of higher valence into ions of lower valence proceeds, which latter react anew with the organic substance etc. Such ions are sometimes called "hydrogen carriers" [13].

The salts of metals which belong to the other group (salts of zinc, mercury, lead and others) have another mechanism of action which consisted in precipitation at the cathode and increasing the hydrogen overvoltage, since it is well known that on zinc, mercury and lead the hydrogen overvoltage is great. The addition to the catholyte of salts of zinc, mercury, lead, can, for example, permit the reduction of nitrobenzene into aniline with excellent yields even at cathodes with low overvoltages where, in the absence of catalytic additives, the evolution of hydrogen [14] will chiefly proceed.

However, the question of the mechanism of action of these catalytic additives has still not been entirely clarified. For example, it is well known that upon the introduction into the catholyte of copper salts or powdered copper a marked increase in the effectiveness of the reduction of aromatic nitrocompounds occurs. This is explained by the fact that copper and also zinc or tin can be precipitated on the cathode and chemically reduce the nitrocompound to amine. Since in the reduction of aromatic nitrocompounds the most difficult stage which determines the rate of the entire process as a whole, is the conversion of the phenylhydroxylamine into the corresponding amine, it is assumed that zinc, tin or copper, precipitated at the cathode, specifically reduce phenylhydroxylamine, thereby increasing the rate of the process as a whole. The absence of complete clarity in the question of the influence of added salt on the process of electroreduction impelled us to study this question in the case of the nitrobenzoic acids. Particular attention was paid to the establishing of a relation between the yields of aminobenzoic acids by substance and the character of the deposits of metallic copper on the cathode. The cathodes were prepared from copper and graphite. The results of the experiments are presented in Table 2.

TABLE 2

Influence of Additions of Cuprous Chloride on the Yields of Aminobenzoic Acids by Substance on Copper and Graphite Cathodes

Concentration of $CuCl_2 \cdot 2H_2O$ (in g)	Yield of acids (in %)					
	o-Aminobenzoic		m-Aminobenzoic		p-Aminobenzoic	
	Cu (30°)	C (40°)	Cu (60°)	C (40°)	Cu (70°)	C (60°)
0	65.3	42.6	63.5	69.9	56.3	67.2
1	73.2	72.8	84.3	83.3	78.4	76.1
3	85.9	73.9	78.0	79.4	80.5	81.5
5	83.2	78.3	79.7	79.1	80.3	79.8
7	—	77.6	78.5	78.7	78.2	84.7

As has already been indicated, the introduction of additions of $CuCl_2 \cdot 2H_2O$ lowers the yield by current, since it increases the quantity of electricity consumed for the evolution of copper from the solution; consequently the introduction of additions of $CuCl_2 \cdot 2H_2O$ is expedient only in those cases when the effect in increasing the yields by substance justifies the additional consumption of electric energy. It is evident from Table 2 that in the majority of cases there exists some limit on the quantity of cuprous chloride introduced into the catholyte, above which no further increase in the yields of aminobenzoic acids by substance occurs. This is apparently explained by the fact that the duration of the electrolysis increases due to the time which is necessary to precipitate the copper from the solution. The increase in the duration of the electrolysis is associated with the emergence of undesirable side processes, in which intermediate and final products of the reduction of nitrobenzoic acids participate and which is associated with the observed reduction in the yields by substance on increase in the quantity of $CuCl_2 \cdot 2H_2O$ introduced into the catholyte.

3. Study of the Influence of the Concentration of Hydrochloric Acid. The data which characterize the yields of aminobenzoic acids at various concentrations of hydrochloric acid, are presented in Table 3.

In the majority of cases the change in the concentration of HCl is not appreciably reflected in the yields of aminobenzoic acids. Only o-nitrobenzoic acid appears to be an exception; during its reduction on a graphite cathode a fall in the yields of o-aminobenzoic acids with increase of HCl concentration is observed; at the same time a considerable quantity of side products appears in the catholyte. Evidently, this is 5-hydroxyanthranilic acid [15].

4. Study of the Influence of Current Density at the Cathode. The current density, as is well known, is an important factor on which very often depends the direction of the electroreduction process, and consequently, the nature of the end product.

The data of the influence of current density on the yields of aminobenzoic acids are presented in Table 4.

As is evident from the data of Table 4, the yields of aminobenzoic acids only slightly depend on the current density when tin and amalgamated zinc are used as the cathodes. This indicates the great rate of reduction of nitrobenzoic acids at a tin cathode, apparently due to the reaction $Sn^{++} \rightarrow Sn^{++++}$, i.e., due to chemical reduction.

TABLE 3

Yields of Aminobenzoic Acids by Substance at Various Concentrations of HCl on Various Cathodes

Concentration of HCl (N)	o-Aminobenzoic Acid					m-Aminobenzoic Acid					p-Aminobenzoic Acid			
	Sn (50°)	Pb (40°)	Zn + Hg (50°)	Cu (30°)	C (40°)	Sn (60°)	Pb (60°)	Zn + Hg (50°)	Cu (60°)	C (40°)	Sn (70°)	Pb (70°)	Cu (60°)	C (70°)
0.58	98.3	76.1	92.5	87.4	87.5	95.7	83.9	91.4	65.6	81.9	94.0	81.4	74.6	82.0
1.16	98.8	79.2	94.4	90.7	82.3	96.5	84.9	92.3	63.2	81.8	94.1	86.1	76.3	82.8
1.74	97.7	86.5	97.9	89.9	78.6	96.1	85.1	95.0	69.2	82.3	94.1	84.5	78.6	83.0
2.32	99.0	88.2	97.4	85.9	78.3	97.2	85.8	95.0	84.3	83.3	94.6	87.9	80.5	84.7
2.9	97.9	85.2	97.7	86.6	71.3	97.0	85.3	95.1	84.0	82.7	94.7	87.5	82.4	85.4
3.48	96.1	84.1	98.0	85.8	70.0	97.1	82.4	94.3	91.4	82.4	94.9	90.7	81.4	85.3
4.06	95.4	82.8	96.7	85.7	–	95.2	82.2	95.4	94.4	82.7	95.3	93.7	82.4	80.3

TABLE 4

Yields of Aminobenzoic Acids by Substance at Various Current Densities on Various Cathodes*

Current density at the cathode A/dm²	Yield of acids (in %)													
	o-Aminobenzoic					m-Aminobenzoic					p-Aminobenzoic			
	Content of HCl (N)													
	2.32	2.32	2.32	1.16	0.58	2.32	2.32	2.32	4.06	2.36	2.32	4.06	2.9	3.48
	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Cu	C
2	95.4	70.8	95.9	72.5	58.1	90.6	70.6	93.2	94.3	66.2	93.4	83.0	79.0	–
4	96.8	87.4	98.6	90.4	75.8	94.2	72.3	93.9	94.3	72.9	94.8	87.1	72.6	81.1
6	98.5	86.3	98.1	91.2	84.8	95.3	74.2	93.6	97.7	81.5	94.2	93.4	73.6	87.2
8	99.0	88.2	97.3	90.7	87.5	97.2	85.8	95.0	94.4	83.3	94.6	93.7	82.4	85.3
10	98.3	84.1	97.2	86.3	86.6	95.6	83.1	95.4	93.5	83.3	94.7	94.3	81.6	81.9
12	95.5	83.4	97.5	87.6	90.8	90.9	82.4	95.4	93.9	81.8	98.0	95.0	82.2	82.1
14	92.3	79.8	97.3	72.9	92.0	84.4	81.9	93.9	87.2	79.2	96.0	93.2	80.3	–

* The experiments were carried out at the same temperatures as in Table 3.

As regards a cathode of amalgamated zinc, reduction on it probably proceeds not as a result of the passage of a

polarizing current, but basically due to decomposition of the amalgam. Electrons, freed by the decomposition of the zinc amalgam, enter into the reduction of the organic substance. A portion of the electrons is consumed by the evolution of hydrogen, which was also observed by us at the time of synthesis. Very interesting results were obtained at the lead cathode. In an already mentioned work [12] the authors reduced p-nitrobenzoic acid at a lead cathode and obtained a maximal yield at a current density of 6A per square decimeter in the presence of 5 g of $SnCl_2 \cdot 2H_2O$.

Increasing the number of rotations of the stirrer by approximately 3 times, we obtained such yields as in the mentioned work, but at a current density of 12A per square decimeter and in the absence of any additive. In the majority of cases diminishing the current density to 2A per square decimeter caused a drop in the yield of aminobenzoic acids due to increase in the electrolysis time and consequently, creation of favorable conditions for the development of side processes. An interesting fact which confirms the existence of a profound relation between the state of the cathode surface and the electroreduction process was noted during the reduction of p-nitrobenzoic acid at a copper cathode. At current densities of 4-6 A per square decimeter in the presence of 3 g of $CuCl_2 \cdot 2H_2O$ a dark precipitate is formed on the copper cathode which is accompanied by lowering of the yield of p-aminobenzoic acid. By reducing the current density to 2A per square decimeter in place of the expected further lowering of the yield an increase in it was observed, in spite of the fact that the electrolysis time was increased in comparison with the preceding experiment (at 4A per square decimeter) by 2 times. The increased yield of p-aminobenzoic acid at 2A per square decimeter, apparently, is facilitated by the dense, bright covering of copper, which is formed on the cathode. The "black" which is formed at the surface of the copper cathode at 4-6 A per square decimeter, probably lowers its activity to some extent.

DISCUSSION OF RESULTS

The results of the study of the process of electroreduction of nitrobenzoic acids under various conditions makes it possible to establish the existence of a relationship between the yields of aminobenzoic acids and the state of the cathode surface. On cathodes of graphite and copper in the absence of additions of $CuCl_2 \cdot 2H_2O$ we did not succeed in obtaining good yields of aminobenzoic acids. The most probable cause of this is the insufficiently high hydrogen over-voltage on copper and graphite. Copper ions, introduced into the catholyte, are destroyed at the cathode with the formation of a metallic precipitate. The effectiveness of the reduction depends on the form of the precipitate. The highest yields of aminobenzoic acids were achieved when a bright sponge having a developed surface, is formed on the cathode. The sponge on the surface of the cathode unmistakably shows catalytic action on the process of electroreduction. The mechanism of action of the sponge can, in our opinion, be represented in the following manner:

1. The finely dispersed sponge can chemically reduce the nitrobenzoic acids to aminobenzoic acids. Lukashevich showed that copper in a finely disperse state is capable of reducing nitrobenzene to aniline [16].

However the role of sponge in the electrochemical synthesis of organic compounds is not exhausted by participation in the process only as a chemical reductant. Lukashevich in the same work reported that finely disperse lead does not have high reducing properties and is capable of reducing nitrobenzene only to phenylhydroxylamine. The rate of the reduction of the latter to aniline is very small. The property of finely disperse lead, established by Lukashevich, clearly does not correspond with the results obtained by us in the electroreduction of nitrobenzoic acids on a spongy lead cathode. In those cases when a lead sponge appears on the cathode, the effectiveness of the reduction is increased and to a greater extent, the greater the volume of the sponge formed. Taking into account the fact that the hydrogen overvoltage on the sponge is less than on a smooth cathode, its role in the processes of electrochemical reduction of organic substances may be determined otherwise than in the first case.

2. In organic syntheses copper in the finely disperse state is widely used as a catalyst [17]. The role of the catalyst consists in lowering the activation energy of the reaction due to adsorption of molecules of the organic substance on the surface of this catalyst. The greater the surface of the catalyst, the higher its capacity for adsorption. During the adsorption there takes place deformation of the molecules of the organic substance which proceeds under the action of the force field of the catalyst surface. The deformation leads to disruption of the bonds in the molecule and to increase in its reactivity [18]. It was established that copper and lead catalyze the reaction of chemical reduction of nitrobenzene into aniline in which the reducing agent is hydrogen. The use of finely disperse lead makes it possible to obtain aniline in a yield equal to 97% [19].

The spongy surface of the cathode responds as well as possible to the demands presented to the active catalysts. On a spongy cathode surface adsorption of molecules of nitrobenzoic acids proceeds and leads to their deformation which is manifested in increase in the dipole moment constant. In a comparison of the dipole moments of many organic substances with the reduction potentials of these substances Voitkevich detected that with increase in the dipole moment the reduction potential becomes more positive, i.e., the depolarizing action of the substance is increased [20]. Thus, increase in the dipole moment which proceeds as a result of the adsorption of nitrobenzoic acid molecules apparently appears to be one of the basic causes of the increase in the effectiveness of reduction on a spongy cathode.

On the basis of the experiments carried out certain conclusions concerning the mechanism of the electroreduction process can be drawn. The concept of taking into account the nature of the cathode material in the processes of electroreduction of organic substances obtained its greatest development in the works of Antropov [21]. By a comparison of the null potential charge of several metals with the reduction potentials of a number of organic substances on cathodes of these metals, Antropov established that the organic depolarizer is well reduced only if the reduction potential is not markedly different from the null potential charge (for example for Zn, Hg, Pb). Antropov explained this situation by the fact that the molecules of the organic substance are adsorbed on the cathode only in the region directly adjacent to the potential of the null charge. If the reduction potential is far removed from the potential of the null charge (Pt, Ag, Ni), the reduction proceeds poorly and is accompanied by the evolution of hydrogen. We have already reported concerning the measurement of the reduction potential of nitrobenzoic acids on various cathodes [22]. It was established that on cathodes of lead, tin and mercury the reduction potentials of nitrobenzoic acids differ little from the null potentials of the charge of these metals. On smooth cathodes of copper and graphite the difference between the reduction potentials and the null potentials of the charge reaches considerable magnitudes. The high effectiveness of the reduction on cathodes of graphite and copper covered with copper sponge, is apparently explained by the fact that as a result of adsorption an increase in the dipole moments of the molecules of nitrobenzoic acids occurs which leads to lowering of the activation energy of the process and which is manifested in diminishing of the reduction potentials and their approximation to the null potentials of the charge of the metals. The reduction of nitrobenzoic acids is, apparently, a primary electrode act which consists in the transfer of electrons from the cathode directly to the electropositive center of the nitrogroup with subsequent participation of hydrogen ions in the formation of the amino group.

SUMMARY

1. The electroreduction process of nitrobenzoic acids to aminobenzoic acids on cathodes of tin, lead, copper, graphite and amalgamated zinc was studied.

2. It was established that the state of the cathode surface plays a substantial role in the electroreduction of nitrobenzoic acids. The maximal yields of aminobenzoic acids were obtained when a lead or copper sponge was formed on cathodes of copper, lead or graphite. It can be assumed that the electroreduction of nitrobenzoic acids on these cathodes is of a catalytic nature.

3. Several assumptions concerning the mechanism of the process of electroreduction of aromatic nitrocompounds were made. The electroreduction process of compounds of this class is, apparently, a primary electrode act.

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