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Electrochemical Oxidation of Organic Compounds on Anodes Consisting of Certain Transition Metal Oxides

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The mechanism and kinetics of the electrochemical oxidation of organic compounds on nickel, cobalt, copper, and silver anodes at potentials corresponding to the formation of the higher oxides of these metals are discussed. The problems of the practical use of the electrodes in the electrosynthesis of organic compounds are examined. The feasibility of different versions of electrosynthetic processes with participation of the higher oxides, regenerated electrochemically, is demonstrated for the nickel oxide electrode.
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I. INTRODUCTION

Electrochemical oxidation reactions of organic compounds on certain transition metal electrodes coated by oxides have been attracting attention in recent years. The studies using these electrodes have been carried out both from the theoretical standpoint in order to investigate the kinetics and mechanism of the oxidation and from the practical standpoint for the assessment of the possibility of using oxide electrodes in the electrosynthesis of organic compounds. Alcohols[1-3], among which di-*O*-isopropylidene-L-sorbose may also be included[4-7], and amines[3] have been oxidised on a nickel oxide electrode, alcohols and amines[8] on a cobalt oxide electrode, amines[9,10] on silver(II) oxides, and alcohols and amines[11] on copper(III) oxides.

II. KINETICS AND MECHANISM OF THE PROCESSES ON ANODES CONSISTING OF TRANSITION METAL OXIDES

The nature of the phenomena occurring on the surface of anodes consisting of a number of transition metal oxides has not yet been completely elucidated. This is why certain views put forward in the literature are contradictory and serve as a basis for further discussion.

The determination of the complete picture of the processes occurring on these electrodes is apparently precluded by the virtual lack of data on the sorption of organic compounds involved in the oxidation reactions, while adsorption phenomena must be taken into account in seeking new procedures for organic electrosynthesis[12].

It has been shown[11] that the mechanisms of the oxidation of alcohols and amines on nickel, cobalt, copper, and silver anodes coated by the oxides are similar and do not involve simple electron transfer, as happens, for example, in the oxidation of amines on graphite.

Potentiodynamic measurements established that the first oxidation stage involves the electrochemical formation of the higher metal oxide and that the entire mechanism can be represented schematically as follows:

$$OH^- + \text{lower oxide} \overset{\text{fast}}{\rightleftharpoons} \text{higher oxide} + H_2O + e; \quad (1)$$

$$(\text{organic substrate})_{soln} \overset{\text{on higher oxide}}{\rightleftharpoons} (\text{organic substrate})_{ads}; \quad (2)$$

$$\text{higher oxide} + (\text{organic substrate})_{ads} \rightarrow \text{lower oxide} + \text{intermediate radical (rate-determining stage)}; \quad (3)$$

$$\text{intermediate radical} - (n-1)e \rightarrow \text{product} \quad \text{or} \quad (4)$$

$$\text{intermediate radical} + (n-1)\,\text{higher oxide} \rightarrow -(n-1)\,\text{lower oxide} + \text{product} \quad (5)$$

here n is the number of electrons involved in the reaction.

For thin oxide layers (particularly on nickel), the equilibrium corresponding to reaction (1) is established rapidly[13], while for thicker layers the diffusion of electroactive species in the film becomes rate-determining[14]. However, according to other data[15] the existence in the oxidation of organic compounds of an equilibrium between the lower and higher nickel oxides, involving nickel hydroxide in the case of thin layers, appears to be doubtful.

Many experimental data[11] support the idea that the organic compounds are oxidised in the adsorbed state on the higher oxide in accordance with reaction (2), although adsorption has not been the subject of a special study and the weak adsorbability of organic substances on iron-group and silver-group metals under analogous conditions has been merely mentioned[16].

The next stage [stage (3)], involving the interaction of the adsorbed organic compound with the higher oxide, was studied in greatest detail, particularly for the nickel oxide electrode. The oxidation of various substances on each electrode proceeds at the same potentials, corresponding to the formation of the higher oxides of the given metal[11]. The mechanism involving a chemical interaction of the organic substance with the higher oxide is indicated by the absence of a dependence of the oxidation current on the potential at low currents and by the dependence of the limiting rate of the electrochemical reaction on the rate of rotation of the disc electrode. Furthermore, a cathodic current is not revealed by the cyclic voltage–current curves for the oxidation process on transition metal oxide anodes in the presence of organic compounds at low rates of application of the potential, and high activation energies for the electrode process have been noted.

To confirm the hypothesis that a chemical reaction mechanism is possible, one can employ data for the chemical oxidation of certain organic compounds by the higher oxides of the same metals. Thus in the oxidation

of alcohols[17] and amines[18] by higher nickel oxides the same products are formed as in the anodic oxidation.

The chemical interaction with the higher oxide probably proceeds in the solid phase and is not associated with the transfer of the metal to the solution, since corrosion of the anode is not observed in the oxidation process. To estimate the rate of chemical interaction of the organic substance with the higher oxide, a study has been made (particularly for nickel) of the time variation of the potential of a non-polarised nickel oxide electrode in the course of its joint reduction by the cathodic current and the compound being oxidised[19]. These results established that the rate of reaction is proportional to the concentration of the organic compound and the amount of the higher oxide on the electrode surface. The calculated chemical oxidation rate constants for certain alcohols are listed in Table 1.

Table 1. The rate constants k for the oxidation of various alcohols on a nickel oxide electrode.

Alcohol	k, mole^{-1} s^{-1}	Alcohol	k, mole^{-1} s^{-1}
Methyl	0.04	Benzyl	0.4
Ethyl	0.06	Furyl	0.8

However, data obtained later by the same authors using the potentiodynamic method[15] conflict, in their view, with the earlier conclusion that the rate of oxidation is proportional to the amount of higher oxide on the electrode surface. According to these data[15], the rate of reaction depends to a considerable degree on the previous history of the electrode. In particular, the rate is greatly reduced on the surface of a nickel oxide electrode which had been subjected to a preliminary oxidation. An increase of the amount of higher oxide of the type NiOOH on the electrode surface has an inhibiting effect on the oxidation reaction. The authors to not rule out the possibility of a direct interaction between the higher nickel oxide and the organic compound but the rate of the reaction must be lower than the rate of oxidation on the fully oxidised surface at potentials which are insufficient for the electrochemical reduction of the oxide layer.

On the other hand, according to other results[11] direct electron transfer in the rate-determining stage is unlikely, since secondary amines are oxidised more slowly than primary amines and tertiary amines are not oxidised at an appreciable rate. This is also confirmed by the occurrence of a kinetic isotope effect in the oxidation of normal and deuterated methanol ($k_{CH_3OH}/k_{CD_3OH} = 7.0$). A similar kinetic isotope effect was observed also in the chemical oxidation of diphenylmethanol by higher nickel oxides ($k_{(C_6H_5)_2CHOH}/k_{(C_6H_5)_2CDOH} = 7.4$).[20]

These results suggest that the rate-determining stage is the abstraction of a hydrogen atom from the molecule of the compound being oxidised with formation of free-radical species [reaction (3)], occurring in the interaction with higher metal oxides. In the chemical oxidation of a series of substances by higher nickel oxides the formation of radicals was confirmed by ESR.[20] A study of the electrochemical oxidation of alcohols to acids on a nickel oxide electrode also established that the rate-limiting stage is the oxidation of the alcohol to the aldehyde[21].

The mechanism of the oxidation of certain organic compounds on a nickel electrode may change depending on the potential, this being related to the degree of oxidation of the electrode surface. At negative potentials the reaction proceeds as a result of direct electron transfer to the smooth nickel electrode or via a dissociative adsorption mechanism[22], while at more positive potentials the oxidation mechanism includes a chemical reaction between the higher nickel oxide and hydrazine[23].

All the above remarks concerning the mechanism of the oxidation of organic compounds on oxide electrodes make it possible to classify the higher oxides of these metals as heterogeneous catalytic transferring agents.

III. ELECTROSYNTHESIS OF ORGANIC COMPOUNDS ON CERTAIN TRANSITION METAL OXIDE ELECTRODES

The data concerning the use of certain transition metal oxide electrodes in the electrosynthesis of organic compounds are few. Table 2 presents comparative results for the oxidation of alcohols and amines on electrodes coated by oxides[11].

Table 2. Current yields of the products of the oxidation of alcohols and amines on anodes coated by oxides.

Starting material	Reaction products	Current yield, %		
		nickel (0.55 V)	silver (0.75 V)	copper (0.7 V)
n-Propylamine	Propionitrile	84	83	85
	Propionaldehyde	11	2	2
n-Butylamine	Butyronitrile	85	85	–
	Butyraldehyde	6	2	–
Isopropylamine	Acetone	80	70	85
Diethylamine	Acetonitrile	46	27	30
	Acetyldehyde	3	3	5
	Acetic acid	36	29	40
Ethanol	Acetic acid	98	–	96
1-Propanol	Propionic acid	95	–	–
2-Propanol	Acetone	90	–	9

The oxidation of alcohols to the corresponding acids in an alkaline medium proceeds on these electrodes with a higher selectivity than in electrolysis in acid solutions on platinum and lead dioxide anodes and makes it possible to avoid esterification reactions, which complicate the process in an acid medium.

Among the electrodes considered, the nickel oxide electrode has been most widely used in the electrosynthesis of organic compounds. It is noteworthy that the specificity of the oxidation on oxide electrodes has also been reflected in the practical application of processes involving higher nickel oxides. There is a fairly wide variety of different ways in which electrosynthetic processes involving higher nickel oxides, regenerated electrochemically in the course of the oxidation, can be carried out. The electrochemical oxidation is performed at an electrode obtained by depositing nickel(II) hydroxide on an inert current-conducting base with subsequent formation of the higher oxide on anodic polarisation[1]. The positive plates of iron–nickel and cadmium–nickel accumulators have also been used as the anodes[5,24–27]. The nickel

oxides may be present in solution as a suspension. Solutions of an alkali[24,25,28,29] or an alkali metal halide[30-39] are used as the electrolyte. In electrolysis in a solution of alkali the higher oxide is regenerated during the transient contact between the solid particle and the current lead. During electrolysis, the current lead is coated by nickel oxides and, as shown below, acquires the properties of a nickel oxide electrode. When the electrolyte is a halide solution, the higher oxide is regenerated both electrochemically and, as in chemical oxidation[17,40], by the interaction with the hypohalite. The oxidation of di-*O*-isopropylidene-L-sorbose (DAS) to di-*O*-isopropylidene-2-oxo-L-gulonic acid (DOGA)—the intermediate in the synthesis of ascorbic acid—has been investigated in detail in the presence of bromides. Under these conditions, the oxidation mechanism can be represented schematically as follows[35]:

$$2\,Br^- - 2e \rightarrow Br_2 \text{ (on the anode)};$$
$$Ni(OH)_2 - e \rightarrow NiOOH + H^+ \text{ (on the anode)};$$
$$Br_2 + 2\,OH^- \rightarrow BrO^- + Br^- + H_2O;$$
$$2\,Ni(OH)_2 + NaBrO \rightarrow 2\,NiOOH + NaBr + H_2O;$$
$$C_{11}H_{17}O_5CH_2OH + 4\,NiOOH + H_2O \rightarrow C_{11}H_{17}O_5COOH + 4Ni(OH)_2.$$

Table 3. The influence of the anode material on the electrochemical oxidation of DAS (0.289 M DAS, 3% NaOH. Q = 1 Ah/g DAS, t = 60°C).

Anode material	Current density, A dm^{-2}	Amount of DAS in soln., g: init.	Amount of DAS in soln., g: residual	Electrode potential, V (w.r.t. normal H e-de)	$NiCl_2 \cdot 6H_2O$, N	Yield of DOGA, %: material: w.r.t. init DAS	Yield of DOGA, %: material: w.r.t. DAS which has reacted	Yield of DOGA, %: material: current	Average current yield of oxygen, %
Nickel foil	5	10.5	1.28	0.9—1.2	0.17	69.0	78.7	30.4	—
	5	9.5	9.5	1.06	—	0	0	0	98
Porous nickel	5	9.7	0.1	0.86—1.0	0.17	84.3	85.0	34.6	—
	5	9.2	6.8	0.7	—	traces		—	85
Nickel oxide*	5	9.7	0.6	—	0.042	91.0	96.0	37.0	—
	5	9.8	1.3	0.7—0.8	—	66.8	77.2	27.6	10—70
Nickel oxide**	5	9.7	0.2	0.72	0.042	96.5	98.5	39.8	—
	5	9.43	0.2	0.67	—	90.2	92.0	35.8	20—98
Nickel oxide*** (lamellar)	30	19.0	10.8	—	—	42.0	98.3	16.4	—
Stainless steel (1Kh13N9T)	5	9.5	0.14	1.28	0.17	87.0	88.0	34.9	—
	5	9.3	8.3	0.94	—	0	0	0	94
Electrode graphite	5	19.7	0.13	1.4	0.17	87.5	88.0	35.5	—
	5	10.0	9.1	—	—	0	0	0	—
Platinum	5	9.7	3.7	1.14	0.17	54.6	88.0	22.4	—
	5	9.5	9.1	1.1	—	0	0	0	95
Lead dioxide	5	12.0	—	—	—	0	0	0	95
Manganese dioxide (thermal)	30	10.1	9.2	1.14	—	0	0	0	95
Cobalt oxide (electrolytic)	30	9.9	9.6	—	—	0	0	0	100
Cobalt oxide (thermal)	30	9.9	8.9	1.06	—	0	0	0	95
Ruthenium oxide (thermal)	5	10.1	10.0	1.25	—	0	0	0	100

* Obtained by a single impregnation of porous nickel initially in nickel chloride solution and then in alkali with subsequent anodic polarisation.
** Factory-made foil electrode.
*** c_{DAS} = 0.58 M.

Higher nickel oxides can be used as chemical oxidants with subsequent electrochemical regeneration in a separate apparatus[41]. Isopentyl alcohol was oxidised in this way to isovaleric acid in 80% yield. The nickel oxide electrode has been most widely used in the electrochemical oxidation of alcohols to the corresponding acids in an alkaline medium, the results obtained in the electrochemical oxidation of DAS being of greatest practical importance.

The electrochemical oxidation of DAS in an alkaline medium has many advantages compared with halide solutions from the standpoint of the yield of the product, the efficiency of the process, and also its cost. Therefore the fundamental characteristics of the electrochemical oxidation of DAS with participation of nickel oxides will be examined only for alkaline solutions. The influence of the electrode material on the electrochemical oxidation of DAS in an alkaline medium has been investigated[25]. The results are presented in Table 3 and in Fig. 1.

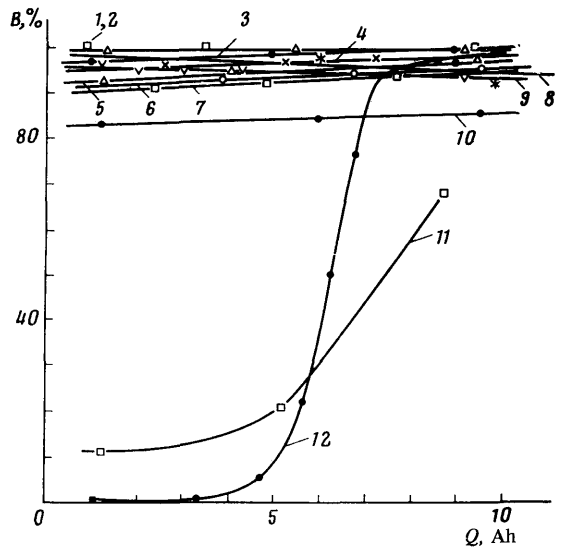


Figure 1. Variation of the current yield of oxygen (B) with the amount of electricity passed through the system in the electrochemical oxidation of DAS on different electrodes: 1) cobalt oxide (electrolytic); 2) ruthenium oxide; 3) nickel; 4) platinum (purified DAS); 5) platinum (technical DAS); 6) cobalt oxide (thermal); 7) stainless steel; 8) lead dioxide; 9) manganese dioxide; 10) porous nickel; 11) nickel oxide (obtained under laboratory conditions); 12) nickel oxide (factory made foil electrode); c_{DAS} = 0.29 M; c_{NaOH} = 3%; t = 60°C; Q = 1 Ah/g DAS.

The current yield of oxygen on nickel, manganese dioxide, lead dioxide, platinum, and stainless steel anodes and also on cobalt oxide and ruthenium oxide electrodes is constant and close to 100%. Accordingly, the consumption of DAS on these electrodes is low (Table 3) and DOGA is not formed.

The electrode potentials at which DAS is oxidised with a low efficiency vary in the range 0.95–1.15 V and there is no definite relation between the electrode potential, the consumption of DAS, and the fraction of the current consumed in its oxidation.

The current yield of oxygen on a porous nickel electrode is 83–84%. DAS is then consumed to an appreciable extent and a small amount of DOGA is formed. A different behaviour has been observed on two nickel oxide electrodes. A considerable proportion of the current was initially consumed in the oxidation of DAS and then, with decrease of its concentration, the current yield of oxygen

rose and reached 100% on an industrial specimen containing a large amount of active mass per unit surface of the electrode. On the second specimen, the fraction of the current consumed in the evolution of oxygen was somewhat higher throughout the experiment and, for the same amount of electricity consumed, the reaction did not reach completion and DAS which failed to react remained. The main oxidation product on nickel oxide electrodes is DOGA, formed in a material yield exceeding 90%. The lower yield of DOGA and the larger amount of DAS which did not react on the lamellar nickel oxide electrode can probably be explained by the poor contact between the solution and the active mass and the consequent decrease of the rate of the chemical interaction.

Comparison of the data for the oxidation of DAS on a smooth nickel electrode, a porous nickel electrode, and three specimens of nickel oxide electrodes makes it evident that the rate of oxidation of DAS increases with increase of the amount of the active mass of the oxides per unit surface of the electrode.

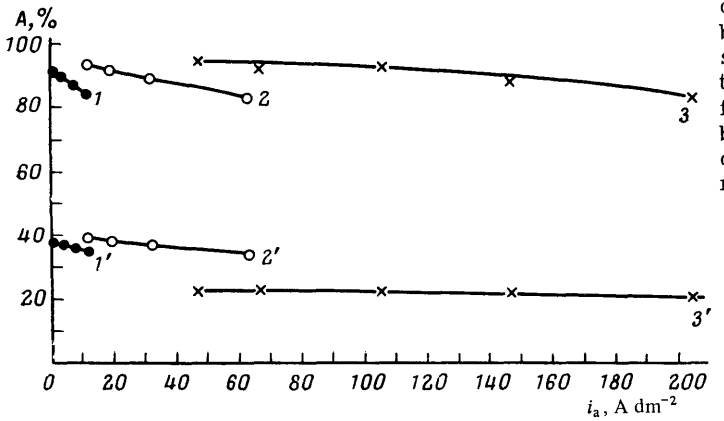


Figure 2. Variation of the yield of DOGA (A) with current density; 0.22 M DAS; 2% NaOH; t = 55°C; Q = 1 Ah/g DAS: 1) and 1′) the material and current yields for coaxially arranged electrodes separated by a distance of 5 mm; 2) and 2′) the material and current yields for horizontally arranged electrodes separated by a distance of 32 mm. 0.4 M DAS; 2.4% NaOH; t = 59°C; Q = 1.72 Ah/g DAS: 3) and 3′) the material and current yields for a vertical arrangement of the electrodes separated by a distance of 25 mm.

The addition of variable-valence metal salts [such as iron(III), cobalt(II), and manganese(II) salts] does not affect the electrochemical oxidation of DAS. The introduction of nickel salts into the solution promotes the formation of DOGA on electrode materials such as smooth nickel, stainless steel, and graphite, on which DOGA could not be obtained in the absence of an additive. The addition of nickel salts increases the yield of DOGA also on nickel oxide electrodes and their effect is more marked on an electrode with a small amount of active mass per unit surface. During electrolysis in the presence of nickel salts, porous electrodes made of different materials become coated by nickel oxides. The presence of nickel compounds on the surface of graphite and in its pores is confirmed by the fact that DOGA is formed even in the absence of an additive on an electrode which had been used beforehand in the presence of nickel salts. In contrast to graphite, the steel electrode remains inactive in subsequent experiments.

The electrosynthesis of DOGA in an alkaline medium on graphite anodes at a current density of 2.4 A dm^{-2} in the presence of dispersed nickel oxides is carried out on an industrial scale using a continuous process[29]. It can be greatly intensified by increasing the current density to 12–15 A dm^{-2}.

It is noteworthy that one of the advantages of the use of nickel oxide electrodes in the electrosynthesis of DOGA is the high rate of the process. Fig. 2 illustrates the influence of current density on the yield of DOGA for different relative positions of the electrodes[5]. When the distance between the electrodes is small, the yield of the product decreases sharply with increase of current density. For a horizontal arrangement of the electrodes and a large distance between them, it is possible to extend greatly the range of current densities without a significant reduction of the material yield of DOGA. At a constant current density the yield depends appreciably on the distance between the electrodes, which can probably be explained by the influence of factors such as the stirring of the electrolyte in the space between the electrodes, the access of the electrolyte to this space, and the filling of the system with gas. For small distances between the electrodes and high current densities, the decisive factor is the filling of the system with gas, which reduces the volume of the reacting solution.

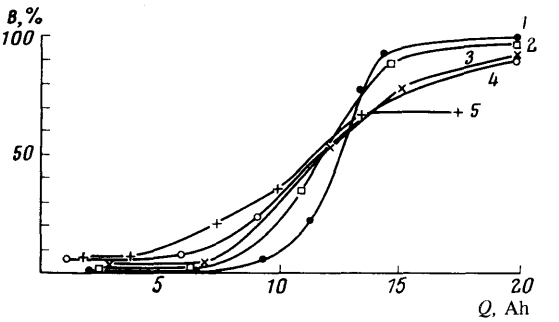


Figure 3. Variation of the current yield of oxygen (B) with the amount of electricity passed through the system at different current densities (Ah dm^{-2}): 1) 5; 2) 10; 3) 21; 4) 29; 5) 50; c_{DAS} = 0.58 M; c_{NaOH} = 3%; t = 60°C.

The optimal conditions for the electrosynthesis of DOGA were established by the simplex design method at a constant current density of 50 A dm^{-2}; then the possibility of carrying out the process at higher current densities was studied under the same conditions. An increase of current density to 100 A dm^{-2} in solutions with high DAS concentrations does not affect appreciably the yield of DOGA (Fig. 2). At higher current densities and a given concentration of alkali the yield falls and the electrode breaks up. The latter is probably associated with the

high rate of the process as a result of which the layer of electrolyte adjoining the anode surface is acidified by the DOGA formed. The change in current density leads to a redistribution of the relative amounts of the current consumed in the electrochemical oxidation of DAS and in the evolution of oxygen (Fig. 3).[24] With decrease of current density, the fraction of the current consumed in the evolution of oxygen falls and the duration of electrolysis increases, which should evidently favour the chemical interaction between DAS and the higher oxides.

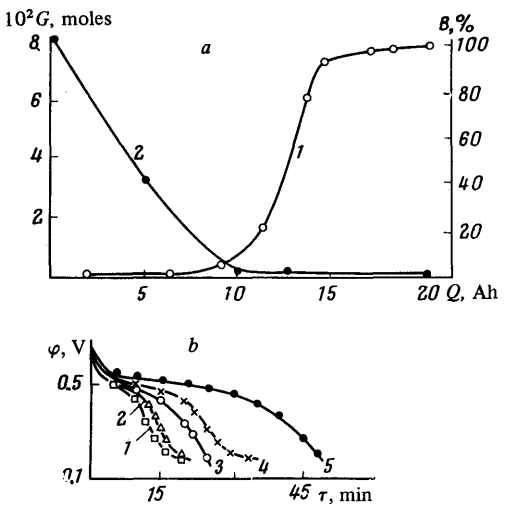


Figure 4. *a*) Variation of the current yield of oxygen (*B*) (curve *1*) and of the amount (*G*) of DAS which failed to react (curve *2*) with the amount of electricity passed through the system; c_{DAS} = 0.58 M; c_{NaOH} = 3%; t = 60°C; i_a = 5 A dm^{-2}; *b*) variation of the potential of a non-polarised nickel oxide electrode with time in 3% NaOH solution at 60°C and different DAS concentrations (M); 1) 0.58; 2) 0.46; 3) 0.35; 4) 0.23; 5) 0.12.

Table 4. The influence of Fe^{3+} ions on the yield of DOGA (c_{DAS} = 0.58 M, c_{NaOH} = 2%, t = 59°C, Q = 1 Ah/g DAS, D_a = 32 A dm^{-2}, $c_{Fe^{3+}}$ = 0.007 M).

No. of expt.	1	2	3	4
Material yield of DOGA, %	91.8	91.6	83.3	81.6
Current yield of DOGA, %	35.8	35.6	32.2	31.6

It is noteworthy that, in the study of the influence of factors such as the concentration of DAS (Fig. 4) and temperature (Fig. 5) on the rate of the process, a correspondence was noted between the changes in the rates of anodic oxidation and chemical interaction. As in an earlier investigation[20], the latter was estimated from the time variation of the potential of a non-polarised nickel oxide electrode discharged in the presence of DAS. Thus the rate of the anodic oxidation of DAS increases with increase of its concentration, the amount of oxides per unit electrode surface, and temperature, and there is a parallel variation of the rate of the chemical interaction of the organic substance with nickel oxides, which may serve as indirect confirmation of their involvement in the oxidation of DAS in the electrolysis, in conformity with the mechanism proposed by Fleischmann et al.[11]

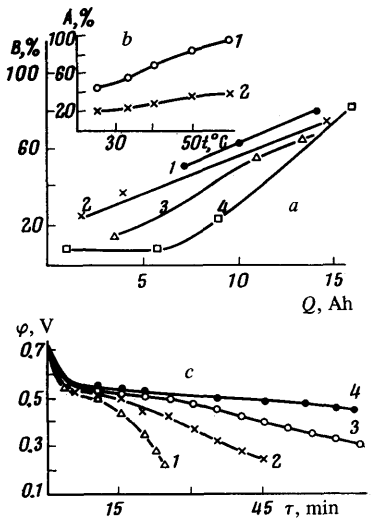


Figure 5. *a*) Variation of the current yield of oxygen (*B*) with the amount of electricity passed through the system at different temperatures (°C): 1) 20; 2) 30; 3) 40; 4) 60; *b*) temperature variation of the material yield of DOGA (*A*) with respect to the DAS introduced (curve *1*) and of the current yield (curve *2*); c_{DAS} = 0.58 M; c_{NaOH} = 3%; i_a = 29 A dm^{-2}; *c*) time variation of the potential of a non-polarised nickel oxide electrode in 3% sodium hydroxide solution at a DAS concentration of 0.35 M and different temperatures (°C): 1) 60; 2) 50; 3) 40; 4) 20.

The extensive experience gained in the use of nickel oxide electrodes in alkaline accumulators has shown that their discharge characteristics are fairly sensitive to inorganic admixtures[42]. The problem of the stability of the active properties of the nickel oxide electrode has also been studied in the electrosynthesis of organic compounds[43]. When the nickel oxide electrode had been used for a comparatively long time, no change in its activity was observed in solutions of purified DAS. Since purification of DAS complicates the technological process and involves loss of product, a study was made of the behaviour of foil and metalloceramic electrodes in the electrochemical oxidation of technical DAS. In contrast to the series of experiments with the purified product, the material yield of DOGA relative to the DAS introduced gradually fell, amounting to 64% on the metalloceramic electrode after the consumption of 2.12×10^3 Ah dm^{-2}, while at the beginning of the series it was 98%. There was a corresponding decrease also of the current yield.

The foil electrode, which contains a smaller amount of active mass per unit geometrical surface of the electrode, loses its activity more rapidly than the metalloceramic electrode. The loss of electrode activity consists in a decrease of the fraction of the current consumed in the electrochemical oxidation of DAS and in an increase of the current yield of oxygen. It has been established that the active properties of the electrode are influenced by inorganic admixtures. Table 4 shows how the yield of DOGA falls gradually under the influence of Fe^{3+} ions.

A similar effect is produced by Ca^{2+} ions. The latter also retard the chemical interaction of DAS and aliphatic alcohols with nickel oxides, which indicates a correspon dence between the rates of the chemical and anodic processes.

The causes of the change in the activity of the nickel oxide electrode are probably analogous to those noted when similar electrodes are used in current sources, their behaviour being determined by the kinetics of the electrochemical oxidation and of the reduction of solid oxides[44], but at much lower current densities.

Different ways of activating nickel oxide electrodes have been investigated. A partial and brief increase of electrode activity occurs after alternate preliminary cathodic and anodic polarisation in a solution of alkali. It is possible to maintain the active properties of the nickel oxide electrode during the electrochemical oxidation of technical DAS by the periodic introduction into the solution of nickel ions (0.01 M), which renews the electrode surface. However, as the electrode continues to be used, the maximum yields are 90–92% after the consumption of $(5.9–6.5) \times 10^3$ Ah dm^{-2} even in the presence of nickel ions, which is somewhat less compared with the results obtained in the absence of additives in the first experiments.

When the electrochemical oxidation of technical DAS on a nickel oxide electrode was carried out with continuous injection of nickel ions (0.004 M), the yield of DOGA remained stable throughout the tests (5.9×10^3 Ah dm^{-2}).

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