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Electrochemical Alkoxylation of Organic Compounds

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The review considers current problems of the electrochemical alkoxylation of heterocyclic compounds, unsaturated and aromatic hydrocarbons, carboxylic acids, amines, and ethers. Certain alkoxydimerisation reactions are also discussed. The methods used to carry out alkoxylation reactions are considered. Much attention is given to the present state of studies on the kinetics and mechanism of electrochemical alkoxylation.
The bibliography includes 120 references.

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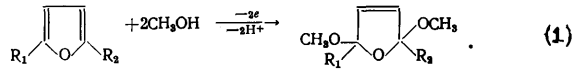
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I. INTRODUCTION

The results of the first experiments on the electrochemical alkoxylation of organic compounds were published at the beginning of the 1950's[1,2]. Over a comparatively short period, numerous studies designed to develop effective electrochemical methods for synthesising a wide variety of alkoxy-derivatives were carried out. Interest in electrolysis as a method for the preparation of compounds of this class is due to the importance of alkoxy-derivatives and also the disadvantages of the chemical methods for their synthesis. Alkoxylated aliphatic and alicyclic organic compounds can be used to synthesise polymers and plasticisers[3-5], valuable lubricating oils[6], emulsifying agents[7], perfumes[8], extractants[9], inhibitors of the oxidation of petroleum products[7], and biologically active preparations[6,10-13].

II. ELECTROCHEMICAL ALKOXYLATION OF HETEROCYCLIC COMPOUNDS

The electrochemical alkoxylation, mainly methoxylation, of furan and its derivatives has been investigated in greatest detail:



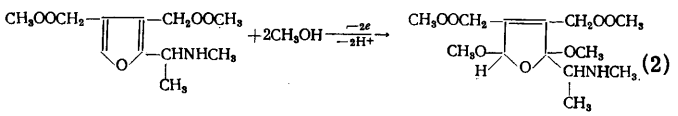
(1)

The electrolysis of a methanol solution of furan (R_1 = R_2 = H) containing ammonium bromide as an electrolyte results in the formation of 2,5-dimethoxy-2,5-dihydrofuran[1,2,14-19], in 92% yield with respect to current, the hydrolysis of which gives a high yield of maleic dialdehyde, a valuable intermediate in the manufacture of synthetic fibres[20].

The electrochemical methoxylation of many α-alkylfurans[21,22], for example silvan (R_1 = H, R_2 = CH_3), and also of disubstituted derivatives such as 2,5-dimethylfuran (R_1 = R_2 = CH_3), which can be converted by methoxylation into a mixture of *cis*- and *trans*-isomers of 2-5-dimethoxy-2,5-dimethyldihydrofuran[22,23], has been studied. The corresponding dimethoxy-derivatives can be obtained by the electrochemical methoxylation of 5-ethyl-2-methylfuran and 2,5-diethylfuran[22].

Electrochemical methoxylation can occur not only as a result of the addition of a methoxy-group, but also as a result of substitution. A characteristic example of reactions of this type is the methoxylation of chloro- and bromo-furans[24]. Apart from reaction (1), substitution by a methoxy-group takes place. The electrochemical methoxylation of 2-bromo- and 2-iodo-furans (R_1 = Br or I; R_2 = H), 5-bromo-, 5-chloro-, and 5-iodo-furfurals (R_1 = Cl, Br, or I; R_2 = CHO), and the methyl ester of 5-bromopyromucic acid (R_1 = Br; R_2 = $COOCH_3$) has been achieved. In all cases the reaction yields trimethoxy-derivatives.

Electrochemical methoxylation takes places with a fairly high efficiency also in the electrolysis of certain other furan derivatives. For example, 2,5-dimethoxy-2,2-dihydrofurfuryl alcohol[21] and 2,5-dimethoxy-2,2-dihydrofurfuryl acetate[18,19,21] can be obtained from furfuryl alcohol (R_1 = H; R_2 = CH_2OH) and furfuryl acetate (R_1 = H; R_2 = CH_2OOCH_3) in yields of 77 and 81—86% respectively. Similarly methoxylation of furfural dimethylacetal [R_1 = H; R_2 = $CH(OCH_3)_2$] at the anode gives a high yield (with respect to the current), of 2,5-dimethoxy-2,5-furfural methylacetal[21]. Methyl pyromucate[25] and some of its derivatives[26-28], for example compounds with R_1 = CH_2NH_2 and R_2 = $COOCH_3$ or with R_1 = $(CH_3)_2CH$ and R_2 = $COOCH_3$, are methoxylated selectively with formation of the corresponding dimethoxy-derivatives. The presence of substituents in the 3- and 4-positions does not hinder the addition of methoxy-groups in the 2- and 5-positions, as can be seen from the following example:

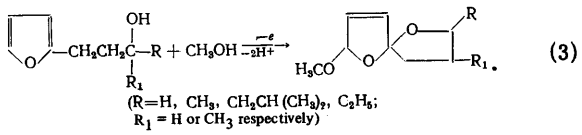


(2)

although the yield in this case does not in fact exceed 50%.[29]

Ponomarev and Markushina[18,19,30-37] investigated the electrochemical alkoxylation of a large group of γ-furylalkanols and showed that, together with the usual addition

of the methoxy group, there is an intramolecular reaction accompanied by cyclisation:

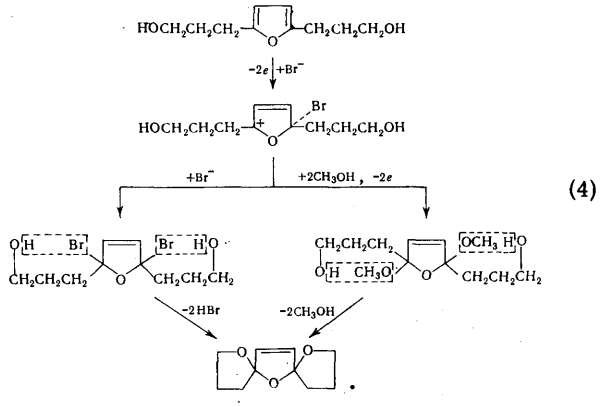


(3)

(R=H, CH_3, $CH_2CH(CH_3)_2$, C_2H_5; R_1 = H or CH_3 respectively)

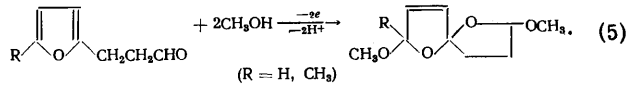
Thus the final products are the corresponding derivatives of 2-methoxy-1,6-dioxaspiro[4,4]non-3-ene. The electrochemical methoxylation of 1-(α-furyl)-3-propanol, 1-(α-furyl)-3-butanol, 1-(α-furyl)-5-methyl-3-hexanol, and a tertiary alcohol—1-(α-furyl)-3-methyl-3-pentanol—has been investigated. Polycyclic spirans are formed on electrochemical methoxylation of mono- and bi-cyclic alcohols[32,36,37]. An attempt at the electrochemical methoxylation of 2,5-di-(3′-hydroxyalkyl)furans led to interesting results[33]. For example, the methoxy-derivative could not be obtained at all from 2,5-di-(3′-hydroxypropyl)-furan. The anodic product of the electrolysis of the compound in methanol containing sodium bromide as the electrolyte is the *trans*-form of 1,6,8-trioxadispiro-[4,1,4,2]-tridec-12-ene.

Intramolecular cyclisation is probably due to the involvement in the reaction of bromide ions and of the hydroxy-group of the initial alcohol. The intramolecular cyclisation reaction may proceed via the following mechanism:



(4)

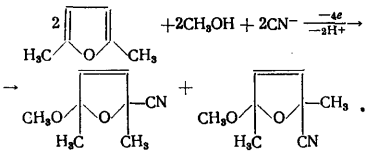
The electrochemical methoxylation of β-carbonyl derivatives of furans is extremely interesting. For example, the electrochemical methoxylation of aldehydes containing the furan ring makes it possible to obtain high yields of derivatives of 2,7-dimethoxy-1,6-dioxaspiro[4,4]non-3-ene[38]:



(5)

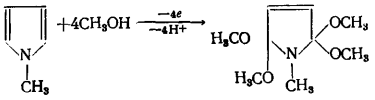
(R = H, CH_3)

The yields of heterospirans vary from 53 to 76%. These products are of interest as biologically active preparations, in particular some of them exhibit a tranquilising activity[38]. If the methanol solution of the heterocyclic compound contains a readily oxidised anion, the electrolysis may be accompanied by the formation at the annode of a product containing two different substituents. For example, the electrolysis of a methanol solution of 2,5-dimethylfuran containing sodium cyanide gives a 74% yield of *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyl-2,5-dihydrofurans[39]:



(6)

Whereas in the electrochemical methoxylation of furan derivatives two methoxy-groups add on as a rule, in the electrolysis of methanol solutions of *N*-methylpyrrole a tetra-substituted derivative is formed at the anode—2,2,5,5-tetramethoxy-1-methyl-3-pyrroline[40]:



(7)

2,6-Dimethoxypyridine undergoes electrochemical methoxylation whereby it is converted into 2,3,5,6-tetramethoxypyridine and 2,3,3,5,6-pentamethoxyazocyclohexa-1,4-diene[40,41].

Several studies have been made on the electrochemical alkoxylation of thiophen and its derivatives[42-44]. The alkoxylation of thiophen is accompanied by the formation of γ-dicarbonyl compounds[42], although in certain cases it is in fact possible to preserve the five-membered heterocycle. For example, 2,5-dimethoxy-2,5-dihydrothiophen can be obtained in 36% yield by the electrochemical methoxylation of thiophen[45]. The methoxylation of methyl 3-(5-methyl-2-thienyl)propionate also involves ring rupture and the formation of a sulphur-free product, which does however contain a methoxy-group: methyl 4,7-dioxo-uct-5-enoate[43]. The electrochemical methoxylation of 1-(3-thienyl)ethyl acetate also involves the removal of sulphur and the formation of 4-acetoxy-3-dimethyoxy-methylpent-2-ene-1-al dimethylacetal (46% yield)[44].

In conclusion, we must consider the alkoxylation of hydrogenated furan and thiophen derivatives—tetrahydrofuran and tetrahydrothiophen[46]. Methoxylation takes place in both cases with formation of α-methoxytetrahydrofuran and α-methoxytetrahydrothiophen in yields of 26 and 8.5% respectively on electrolysis of methanol solutions containing sodium methoxide.

The conditions governing the electrochemical ethoxylation of heterocyclic compounds probably do not differ significantly from those for methoxylation. This is indicated by experiments on the electrochemical oxidation of furan in ethanol[47].

III. ELECTROCHEMICAL ALKOXYLATION OF UNSATURATED AND AROMATIC HYDROCARBONS

Electrochemical alkoxylation of unsaturated hydrocarbons is more selective than the reactions involving heterocyclic compounds. The electrochemical methoxylation of aryl-substituted unsaturated hydrocarbons—styrene and its derivatives[48,49] and stilbene[49,50]—has been investigated in greatest detail. The electrochemical methoxylation of styrene gives a 20% yield of dimethoxyphenylethane[48]:

(8)

α-Methylstyrene and 1,1-diphenylethylene are converted respectively into the dimethyl ether of 1-methyl-1-phenylethylene glycol (15%) and the dimethyl ether of 1,1-diphenylethylene glycol[48] in 23% yield.

The electrochemical ethoxylation of styrene resulted in the formation of methane, ethane, the diethyl ether of styrene glycol, *meso*-1-4-diethoxy-2,3-diphenylbutane, and condensation products of acetaldehyde which the authors[49] believe to be formed as a result of decomposition of ethoxy-radicals. Studies on the electrochemical alkoxylation of stilbene[49,50] indicate the possibility of obtaining a satisfactory yield of dimethoxydiphenylethane.

Benzene does not undergo electrochemical alkoxylation, while its derivatives are methoxylated on electrolysis[51-56]. Benzyl methyl ether, 1-methoxy-1-phenylethane, and α-methoxyisopropylbenzene have been obtained in low yields by the electrochemical methoxylation of toluene, ethylbenzene, and cumene respectively[51]. The reactivity of alkylbenzenes in the alkoxylation reaction decreases in the sequence $C_6H_5CH(CH_3)_2 > C_6H_5C_2H_5 > C_6H_5CH_3$.

Interesting data have been obtained on the electrochemical methoxylation of 9,10-disubstituted anthracene derivatives[53]. On methoxylation of anthracene and 9,10-dimethylanthracene, the ratios of the *cis*- and *trans*-dimethoxy-derivatives are respectively 3:1 and 5:1. If diethyl-, dipropyl-, and diphenylanthracenes are methoxylated, the ratio of the *cis*- and *trans*-isomers changes in favour of the latter, approaching 1:1.

Reactions involving tetralin, indan, and diphenylmethane lead to the formation of the corresponding α-methyl ethers in low yields[55,57]. If the methanol solution of tetralin contains cyanides, then at anodic potentials of about 2.5 V electrochemical cyanation products[54], for example 6-cyanotetralin[56], appear in solution in addition to the methoxy-derivatives.

The electrochemical methoxylation of cycloalkenes yields the corresponding mono- and di-substituted derivatives[58]. For example, 1-methoxycyclohex-2-ene, 1,1-dimethoxycyclohexene[58], and in some cases 3-methoxycyclohex-1-ene[59] may be obtained from cyclohexene, while 1-ethylcyclohex-1-ene can give rise to 1-(1′-methoxyethyl)cyclohex-1-ene, 1-ethyl-3-methoxycyclohex-1-ene, and 2-ethyl-1-methoxycyclohex-2-ene[58]. The methoxylation of 2-methylpent-2-ene gives rise to three products: 3-methoxy-2-methylpent-1-ene, 2,3-dimethoxy-2-methylpent-1-ene, and 2,2-dimethoxypent-2-ene in an overall yield of 71%.[58] 3,4- and 3,6-dimethoxycyclohex-1-enes are formed as a result of the electrochemical methoxylation of cyclohexadiene[60]. A certain amount of the products of the addition of the methoxy-radical in the 1- and 4-positions are observed on electrolysis of the methanol solution of buta-1,3-diene[61,62], although in this case the methoxy-dimerisation reaction, which will be discussed below, is more typical.

As in some of the examples discussed previously, electrochemical methoxylation may result in the formation of bifunctional compounds owing to the addition of two different substituents to the hydrocarbon molecule. For example, electrolysis at the anode of methanol saturated with hydrogen chloride and ethylene results in the formation of chloromethoxyethane together with dichloroethane[63,64]:

$$C_2H_4 + CH_3OH + Cl^- \xrightarrow[-H^+]{-2e} CH_3OCH_2CH_2Cl. \qquad (9)$$

1-Hydroxy-4-methoxybut-2-ene can be synthesised by the electrolysis of a methanol solution of potassium hydroxide containing buta-1,3-diene[62,65].

IV. ELECTROCHEMICAL ALKOXYLATION OF COMPOUNDS WITH FUNCTIONAL GROUPS

A number of studies have been devoted to the electrochemical alkoxylation of organic acids. For example, electrochemical oxidation of *exo*- and *endo*-norbornane-3-carboxylic acid in methanol solution yielded methyl *exo*-norbornyl ether, while *exo*- and *endo*-5-norbornenecarboxylic acids give rise to 3-methoxynonatricyclene[66]. Methoxy-derivatives of hydrocarbons are formed in the electrolysis of methanol solutions of organic acids as a result of the replacement of the carboxy-group by a methoxy-group. For example, in the oxidation at the annode in methanol solution of acids with the general formula $o\text{-}XC_6H_4(CH_2)COOH$, where X = Cl, Br, or O_2, the methoxy-derivative $o\text{-}XC_6H_4(CH_2)_nOCH_3$ was detected together with the products of the anodic Kolbe condensation and certain other derivatives[67]. The yield of ether diminishes with increase of *n*. The substitution process can involve also the hydrogen atoms in the side chain. This is characteristic of phenylacetic acids[66]:

$$RC_6H_4CH_2COOH \xrightarrow[-CO_2,\ -H^+]{-2e,\ +CH_3OH} RC_6H_4CH_2OCH_3$$
$$\xrightarrow[-CO_2,\ -3H^+]{-3e,\ +2CH_3OH} RC_6H_4CH(OCH_3)_2$$
$$\xrightarrow[-CO_2,\ -H^+]{-4e,\ +3CH_3OH} RC_6H_4C(OCH_3)_3. \qquad (10)$$
(R=CH$_3$O, N(CH$_3$)$_2$)

The electrochemical alkoxylation of adamantane-1-carboxylic acid in a methanol solution of sodium methoxide results in the formation of 1-methoxyadamantane in 65% yield[68]. Under the same conditions, the methoxylation of adamantane-1-acetic acid leads to 3-methoxyhomoadamantane[69]. If the methanol solution of an unsaturated acid contains hydrogen chloride or bromide, then chlorine or bromine adds to the double bond together with the methoxy-group. Thus α-chloro- or α-bromo-β-methoxyphenylpropionic acid can be obtained from cinnamic acid[70]. Methoxylated products were detected also in the anodic Kolbe condensation of ω-hydroperfluorovaleric and ω-hydroperfluorooenanthic acids[71]. The principal products of the anodic oxidation of certain α-ketoacids RCOCOOH in methanol solutions are the methyl esters $RCOOCH_3$ (R = CH_3, C_2H_5, or n-C_3H_7), which are formed in yields of 65—81.5%.[72] The yield of esters increases in the following sequence in terms of R: $CH_3 > C_2H_5 >$ n-C_3H_7.

The possibility of the methoxylation [part of the Russian text is missing at this point (Ed. of Translation)].....the yield of methoxydioxan is 28%.[46]

Among nitrogen-containing organic compounds, most attention has been devoted to the alkoxylation of amines[17,40,73,74]. Electrochemical methoxylation of *NN*-dimethylaniline gave a mixture[46] of *N*-methoxymethyl-*N*-methylaniline and the product of more extensive alkoxylation—*NN*-(dimethoxymethyl)aniline—in proportions of 6:1:

$$C_6H_5N(CH_3)_2 \xrightarrow[-H^+]{-e,\ +CH_3OH} C_6H_5N(CH_3)(CH_2OCH_3) \xrightarrow[-H^+]{-e,\ +CH_3OH} C_6H_5N(CH_2OCH_3)_2 \qquad (11)$$

Similarly one can synthesise α-methoxy-*NN*-dimethylbenzylamine and *N*-methoxymethyl-*N*-methylbenzylamine from *NN*-dimethylbenzylamine and 3-methyl-2-phenyloxazolidine, 3-benzyloxazolidine, and *N*-methoxymethyl-*N*-methylbenzylamine from *N*-benzyl-*N*-methylethanolamine[40,74]. The electrochemical methoxylation of

cyclohexyl isocyanate takes place with a low yield of methoxylated products (20%) and seven different compounds, five of which proved to be methoxides, were identified in the mixture[74].

A few studies have been made on the electrochemical methoxylation of ethers. For example, in the electrochemical methoxylation of the dimethyl ether of resorcinol, 2,3,3,6,6-pentamethoxycyclohexa-1,4-diene is formed in 61% yield[76]. However, veratrol is methoxylated at the anode with a lower selectivity and yields four substances, including hexamethyl *cis,cis-o*-muconate—the product of the opening of the benzene ring[76]. In the electrochemical methoxylation of anisole[41,77] in an alkaline solution, *o*-, *m*-, and *p*-dimethoxybenzenes are formed in proportions of 39 : 3 : 58.[41] The reaction in an acid medium takes place in a more complex manner[77]. In this case, the electrolysis products are the methyl esters of *p*-methoxybenzoic (45.3%) and *o*-methoxybenzoic (4.5%) acids as well as the dimethyl esters of maleic (15.5%) and succinic (23.8%) acids.

The electrochemical alkoxylation of trimethylsilane has also been described[78]. The yield of alkoxytriethylsilane in the electrolysis of an ethanol solution of triethylsilane varies in the range 30—80%. Attempts at electrochemical alkoxylation in *t*-butyl alcohol were unsuccessful.

V. ELECTROCHEMICAL ALKOXYDIMERISATION

In some cases electrochemical alkoxylation is accompanied by dimerisation with formation of dimethoxy-derivatives of compounds with twice as many carbon atoms as the starting material. For example, a dimeric product—*meso*-1,4-diethoxy-2,3-diphenylbutane—is formed in the electrolysis of an ethanol solution of styrene at the anode together with the ethoxylation product (the diethyl ether)[49,79]:

$$2C_6H_5CH{=}CH_2 + 2C_2H_5OH \xrightarrow[-2H^+]{-2e} C_6H_5CH(OC_2H_5)-CH_2CH_2-CH(OC_2H_5)C_6H_5. \quad (12)$$

The electrolysis of a methanol solution of *cis*-cyclopropane-1,2-dicarboxylic acid results in the formation of a mixture of dimeric products—dimethyl ester of bicyclopropyl-2,2-dicarboxylic acid and the methyl ester of cyclopropane-1,2-dicarboxylic acid[80]. A number of studies in recent years were specially undertaken to investigate the conditions governing the alkoxydimerisation reaction and the methods for the electrochemical synthesis of alkoxydimers[61,62,65,79,81,82].

Electrochemical methoxylation of buta-1,3-diene can give rise under certain conditions to three isomeric dimethoxyoctadienes[79,83]: *trans, trans*-1,8-dimethoxyocta-2,6-diene, *trans*-1,6-dimethoxyocta-2,7-diene, and 3,6-dimethoxyocta-1,7-diene. In other investigations[61,62,65], 1,6-dimethoxy-2-vinylhex-4-ene was detected in addition to the first isomer. However, the product yields do not exceed 15%. Apart from the products mentioned, two isomeric dimethoxydodecatrienes were detected in an overall yield of 11%.[83] Methoxydimers are obtained in somewhat higher yields in the electrolysis of arylated olefins—styrene, α-methylstyrene[83], and isoprene[84]—as well as vinyl ethers[81,85]. In the last case, the reaction has been investigated for a fairly large number of systems:

$$2R_1O-\underset{R_3}{\overset{}{C}}=\underset{R_4}{\overset{}{C}}-R_2 + 2R_5OH \xrightarrow[-2H^+]{-2e} R_1O-\underset{R_3}{\overset{OR_5}{C}}-\underset{R_4}{\overset{R_2}{C}}-\underset{R_4}{\overset{R_2}{C}}-\underset{R_3}{\overset{OR_5}{C}}-OR_1, \quad (13)$$

where $R_1, \ldots, R_5$ are C_nH_{2n+1} groups with $n = 1-8$ for R_1, $n = 0-8$ for R_2-R_4, and $n = 1-4$ for R_5; R_1 can also be a five- or six-membered cycloalkyl group.

Together with dimerisation, there is simple addition of alkoxy-groups to the double bond. The yield of products then exceeds the yield of methoxydimers, although in some cases, for example, for ethyl vinyl ether, it reaches 51%.[83]

A methoxydimer—1,1-dimethoxy-2,2′-bisindanyl—can be obtained in 38% yield by the anodic oxidation of indene in methanol[83].

Finally, we must consider the anodic coupling reaction with formation of dimethoxy-derivatives occurring when alcoholic solutions of two different unsaturated hydrocarbons are electrolysed[82]. For example, the electrolysis of a methanol solution of styrene and ethyl vinyl ether results in the formation of a methoxydimer—4-ethoxy-1,4-dimethoxy-1-phenylbutane:

$$C_6H_5CH{=}CH_2 + H_2C{=}CHOC_2H_5 + 2CH_3OH \xrightarrow[+2H^+]{-2e} C_6H_5CH(OCH_3)-CH_2CH_2-CH(OCH_3)OC_2H_5, \quad (14)$$

1-Ethoxy-1,4-dimethoxy-4-phenylpentane has been synthesised in this way from α-methylstyrene and ethyl vinyl ether.

VI. CONDITIONS GOVERNING THE ALKOXYLATION AND ALKOXYDIMERISATION REACTIONS

The mode of the alkoxylation reaction and the nature and yields of products depend largely on the nature of the anode material, the electrolyte, the concentrations of the initial organic compounds, the current density, the anode potential, and the solution temperature. Systematic studies designed to compare the roles of these factors have not been made. However, certain largely qualitative generalisations can be made from the available data.

Electrochemical alkoxylation and alkoxydimerisation have been carried out at anodes made of platinum[17,22,23,40,48-50,52,54,55,57,58,60-62,65,68,73,74,76,85] and charcoal or graphite[5,18,19,24,30-38,43-46,75,79,82,83]. Platinum[66,74], graphit[82], nickel[18,19,40,43,61,62,65,47] or mercury[22,60] have been used as the cathode materials. Probably in the electrochemical alkoxylation of heterocyclic compounds, fairly high yields of products may be achieved at both platinum and graphite anodes. On the other hand, in the vast majority of the experiments on the electrochemical alkoxylation of hydrocarbons and organic compounds with functional groups platinum anodes were used.

The choice of electrolyte constitutes a very important problem. Electrochemical alkoxylation of heterocyclic compounds takes places most efficiently in alcoholic solutions of bromides, mainly ammonium bromide. Attempts to employ as electrolytes alcoholic solutions of nitrates, carboxylic acid salts, and sulphuric acid inevitably resulted in a lower yield of alkoxy-derivatives. The specific role of bromide in the electrochemical alkoxylation of heterocyclic compounds has been discussed by a number of workers[2,24,33,41]. Alcoholic solutions of alkalis and alkoxides can be recommended for the electrochemical alkoxylation of hydrocarbons[49,61,62,65] and tertiary amines[17]. Attempts to employ bromides as electrolytes in the electrochemical alkoxylation of unsaturated hydrocarbons lead to the formation of bromo-derivatives.

An important process parameter is the anodic current density. Electrochemical alkoxylation is carried out over

a fairly wide range of anodic current densities—from 1 to 10 A dm^{-2}. The ratio of the alkoxylation and alkoxydimerisation products depends to a considerable degree on the anodic current density when these reactions can occur simultaneously. Experimental data show that the yield of alkoxydimerisation products as a rule increases with decrease of anodic current density. Anodic current density can also influence the proportions of the isomers of the alkoxydimers. For example, in the electrochemical methoxylation of buta-1,3-diene an increase of anodic current density entails an increase in the yield of the linear dimer 1,8-dimethoxyocta-2,6-diene in a mixture with the branched isomer 1,6-dimethoxy-2-vinylhex-4-ene[62].

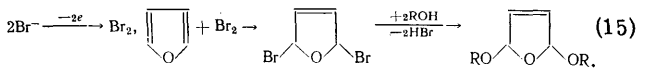
The mode of reaction is influenced significantly by the concentration of the initial organic compound. As a rule, when the alkoxylation reaction is accompanied by alkoxydimerisation an increase in the concentration of the initial organic compound tends to increase the rate of the latter[62].

Finally, we must consider the effect of the temperature of the solution electrolysed. In most cases, it is recommended that the electrolytic alkoxylation of heterocyclic compounds be carried out at low temperatures ranging from −20°C [1,14] to 25°C.[43] It is also useful to maintain low temperatures (between −10° and −15°C) when low-boiling reagents (for example buta-1,3-diene) are involved in the reaction in order to reduce their volatility and increase their solubility. It is not recommended that the alkoxylation and alkoxydimerisation reactions be carried out above 20—25°C, although the methoxylation of cyclohexyl isocyanate in the electrolysis of boiling methanol containing sodium methoxide has been described[75].

VII. THE MECHANISMS OF THE ALKOXYLATION AND ALKOXYDIMERISATION REACTIONS

The number of studies on the mechanisms of the alkoxylation and alkoxydimerisation reactions is much smaller than on their preparative applications. In the published studies, the mechanism of electrochemical alkoxylation is generally regarded as an aspect of the electrode processes (the nature of the primary stage, the adsorption of the reactants, etc.) or is treated from the standpoint of secondary chemical reactions (the mode of addition and substitution, structural effects, etc.). Studies dealing in detail and systematically with the problems of the secondary and primary reactions in electrochemical alkoxylation and alkoxydimerisation have not yet been made. The literature data on this question are often highly contradictory. This is largely caused by experimental difficulties, which are inevitable when electrochemical methods are employed to investigate the kinetics of electrode processes in non-aqueous media. Significant difficulties arise also owing to changes in the surface of the anode over a period of time—a specific deactivation effect is characteristic of many anodic alkoxylation processes[44,62,80]. Electrochemical measurements are limited as a rule to the recording of polarisation curves[17,74,86,87]. On the other hand, the interpretation of the mechanism solely on the basis of an analysis of stable electrolysis products, which is done in the majority of investigations[41,88], makes the reaction mechanisms thus devised somewhat arbitrary[88,89]. As a result the mechanisms of the alkoxylation and alkoxydimerisation reactions remain on the whole to a considerable degree controversial. We shall consider certain modern ideas in this field.

The generally accepted view is that the alkoxylation reaction proper is the secondary chemical reaction which follows the discharge of the electrochemically active species at the electrode. However, different investigators hold divergent views concerning the nature of this species. As already mentioned, in the first studies on the methoxylation of furan, it was established that the reaction takes place most efficiently when bromide salts are employed as the electrolytes. On this basis, it was concluded in a number of investigations[2,5,15,19,24,33], that the initial reaction stage is the discharge of the bromide ion. This view is held, for example, by Ponomarev and Markushina[9,33], who suggest that the alkoxylation of furan derivatives proceeds via three stages. The first involves the oxidation of the bromide ion with formation of molecular bromine, in the second bromine undergoes 1,4-addition to the ring, and in the third dibromohydrofuran is alkoxylated chemically with elimination of HBr:



(15)

Kochetkov et al.[90] assume an analogy with chemical alkoxylation in the presence of bromine, where the initial stage is two-step electrophilic addition of Br_2. Sokolov and Giller believe that the primary step in the electrochemical methoxylation of furans in the presence of ammonium bromide is the formation of atomic bromine and its subsequent recombination to molecular bromine, which is in fact responsible for the methoxylation proper in the bulk of the solution[24]. A similar point of view has been largely adopted in studies by certain Japanese investigators[52], who assume that the discharge of the anion, regardless of its nature, is the initial reaction step. In contrast to the previous mechanism, Japanese investigators believe that the process may be described by the following consecutive reactions:

$$X^- \rightarrow X^\cdot + e\,(A);\ RH + X^\cdot \rightarrow HX + R^\cdot \quad (B)$$
$$CH_3OH \rightarrow CH_3O^\cdot + H^+ + e\,(C);\ R^\cdot + CH_3O^\cdot \rightarrow CH_3OR\ (D). \qquad (16)$$

It is suggested that reaction (16B) is rate-determining. A characteristic feature of this mechanism is the electrochemical step involving the anodic oxidation of an alcohol molecule with formation of a $CH_3O\cdot$ radical. Methoxylation takes place homolytically as the recombination of $CH_3O\cdot$ and a radical formed from the substrate molecule via reaction (16B). Possibly in some cases, for example in halogen-containing electrolytes, this mechanism is acceptable but it can hardly be general. In fact the yield of methoxy-derivatives of furan is higher in solutions of bromide salts, but these derivatives are formed also in electrolytes containing NH_4NO_3, $NaNO_3$, sodium formate[17,91], sulphuric acid[61,62,91], alkalis[52,65,84], boron trifluoride-ether[91], cyanides, perchlorates[39,52,74], and other compounds[52]. The discharge of the anions of such electrolytes, for example ClO_4^-, F^-, etc., requires much higher positive potentials than those which actually obtain in the alkoxylation or alkoxydimerisation reactions. Naturally the step (16C) is ruled out when the electrolyte is a methoxide. Thus the mechanisms postulating as the initial step the direct electrochemical oxidation of the alcohol at very low positive potentials are more acceptable and undoubtedly more general.

Regardless of the conflict between the views concerning the nature of the electrochemical stage, the involvement of the methoxy-radical in the reaction is postulated by the

vast majority of investigators. However, the assertion that the electrochemical oxidation of alcohols generates the corresponding alkoxy-radicals is frequently made without sufficient evidence, solely on the basis of the observed formation of ethers. An attempt at a quantitative approach to this problem was made by Tsutsumi and coworkers[51], who showed that the relative reactivities of many aromatic compounds in electrochemical alkoxylation is fully consistent with Szwarc's observations[92] on their behaviour in free-radical reactions. A further development of this approach, within the framework of mechanism (16), is illustrated by the work of Sasaky et al.[52], who investigated the reactivity of alkylbenzenes in the electrochemical synthesis of α-substituted methyl ethers under various conditions. They established a linear relation between the current yield and the heat of reaction (16B) (rate-limiting step) calculated from thermochemical data. They believe that this finding is consistent with Semenov's law of the proportionality between the activation energy and enthalpy[93] for radical reactions and therefore confirms the validity of the homolytic mechanism. Since such views have gained wide acceptance recently[55,94], note should be taken of the methodological error which they involve.

In the first place the current yield of methoxy-derivatives in various electrolytes cannot be regarded as equivalent to the relative reactivity (the rate constant for the reaction between X· and RH), since the rate of formation of X· and their "actual" concentration determined by the partial oxidation current [stage (16A)] are not taken into account. Since the potential was not measured in the electrolysis and the reaction was carried out galvanostatically, the feasibility of reaction (16A) in all the cases investigated (X^- = F^-, ClO_4^-, OH^-, Cl^-, etc.) becomes doubtful. The application of concepts of homogeneous kinetics to this reaction, which the authors themselves regard as heterogeneous[52], also appears incorrect.

It is not the first time that attempts have been made in the literature to employ thermochemical data in order to establish the mechanisms of electrode reactions. The error of this approach has been demonstrated by Conway and Vijh[95]. Moreover, the validity of the "Semenov—Polanyi rule" cannot alone be regarded as a criterion of the validity of the homolytic mechanism, since it is a special case of the Brønsted equation or "the principle of the linearity of free energies", which is valid for many classes of chemical reactions regardless of their mechanism[96]. The above critical comments do not, however, refer to the actual conclusion that the stage involving the formation of the ether is homolytic. This conclusion is adhered to by the majority of investigators of this reaction. According to Inoue and Tsutsumi[48], only homolytic substitution can result in the formation also of certain side products of the oxidation of alkylbenzenes in alcoholic media, for example dimeric compounds.

The possibility of forming alkoxy-radicals was confirmed in a study[97] of the oxidation of tertiary alcohols of the type $R_1R_2(C_6H_5)COH$ (R_1 and R_2 = CH_3, C_2H_5, and iso-C_3H_7). The authors of this investigation, who carried out the electrolysis in aqueous dioxan solutions of the alcohols, observed a high yield of ketones (80—90%) and detected dimeric gaseous products. These products were interpreted as resulting from the formation of t-alkoxy-radicals by the reaction

$$R_1R_2PhCOH \xrightarrow[-H^+]{-e} R_1R_2PhCO^{\cdot}. \qquad (17A)$$

Next, decomposition into ketone molecules and aliphatic radicals takes place:

$$R_1R_2PhCO^{\cdot} \begin{cases} \longrightarrow R_1COPh + R_2^{\cdot} \\ \longrightarrow R_2COPh + R_1^{\cdot}, \end{cases} \qquad (17B)$$

which then recombine or disproportionate according to the equations

$$R_1^{\cdot} + R_2^{\cdot} \begin{cases} \longrightarrow R_1R_1 + R_2R_1 + R_2R_2 \\ \longrightarrow R_1H + R_2H + \text{olefins}, \end{cases} \qquad (17C)$$

The intermediate formation of an alkoxy-radical in the reaction involving furan is also postulated in the electrolysis of solutions containing non-halide electrolytes[22,60].

Despite the fact that a homolytic mechanism is assumed in most investigations, there are also discrepancies as to the details of the process (if these are considered at all). Thus in many studies it is assumed that, under the conditions of electrolytic alkoxylation, the alcohol is oxidised in the molecular form[51,52,76,94]. However, comparative analysis of polarisation measurements and of the composition of the electrolysis products in the anodic methoxylation of tertiary amines in various electrolytes led to the conclusion[74] that the active species in the electrochemical stage proper is only the methoxide ion. The possibility of oxidising the alcohol at the anode in both molecular and anionic forms, depending on the acidity of the medium, is indicated by experiments on the alkoxylation of 1,3-dienes[84,98].

In early and also in certain recent investigations, the problem of whether the reaction is homogeneous or takes place on the surface of the electrode was ignored. Recently several special investigations on this question were made[17,40,52].

Sasaky et al.[99], who investigated the oxidation of methanol in the presence of $NaClO_4$, NaOH, and $NaOCH_3$ as supporting electrolytes, concluded that the methoxy-radical may diffuse far from the surface of the anode. This conclusion is based on the finding that the electrochemical oxidation is accompanied by the evolution of gas at the porous diaphragm separating the cathodic and anodic compartments. This fact is interpreted as follows:

$$CH_3OH_{ads} \rightarrow CH_3O^{\cdot}_{ads} + H^+ + e, \qquad (18A)$$

$$CH_3O^{\cdot}_{ads} \rightarrow CH_3O^{\cdot}_{bulk}, \qquad (18B)$$

$$2CH_3O^{\cdot} \xrightarrow{\text{disproportionation}} CH_3OH + HCHO. \qquad (18C)$$

However, these results were not confirmed by any other investigator. The mechanism proposed by Sasaky et al. can hardly be regarded as probably bearing in mind the instability of free $CH_3^{\cdot}$ radicals. The fact that the reaction

$$CH_3O \rightarrow HCHO + H \qquad (18D)$$

is endothermic [q = (−20)—(−40) kcal mole^{-1}] [93] is hardly an unambiguous indication that CH_3O· has sufficient stability for reactions (18B)—(18C), to occur as suggested by Sasaky et al.[99] Indeed, mechanism (18) itself shows that reaction (18D) does not constitute the only pathway for the removal of methoxy-radicals.

Many data indicating the formation of intermediate adsorbed radical products in the electrochemical oxidation of alcohols have been published[100-102]. The problems of the structure of these species have been the subject of special investigations in recent years by potentiostatic, galvanostatic, potentiodynamic, and radiochemical measurements[88,101-103]. However, these measurements were

made mainly in dilute aqueous solutions which precludes an unambiguous extrapolation of the results to alkoxylation conditions. This problem requires special consideration.

The oxidation of lower aliphatic alcohols in aqueous solutions up to high concentrations[100] has been intensively investigated in recent years in connection with the problem of fuel cells. As emphasised previously[88], the results of these investigations probably cannot be used for an unambiguous interpretation of the electrode processes in alkoxylation owing to the significant differences in reaction conditions. However, it would also be a mistake to ignore them completely (as is done in many investigations of the electrochemical alkoxylation), particularly since electrochemical synthesis of alkoxy-derivatives can take place also in aqueous alcoholic media[98].

A unanimous view on the mechanism of the anodic oxidation of alcohols in aqueous solutions does not exist either[101-103]. Electrochemical measurements at the electrode—alcohol solution boundary indicate the possible adsorption on the surface of the anode of a whole range of carbon-containing species characterised by different bonding energies with the surface. (For example: $\cdot C\begin{matrix}OH\\ \\ O\end{matrix}$, $\ddot{C}{=}O$, $\ddot{C}-OH$, and $\cdot CH_2OH$ in the oxidation of methanol and $CH_3\dot{C}HOH$ and $CH_3CH_2O\cdot$ for ethanol[104]). Some investigators[102] believe that in acid solutions methanol is oxidised via a stage involving the formation of the species $[COH]:_{ads}$. Without special assumptions, such ideas are inconsistent with, for example, the results of the preparative electrolysis of acid alcoholic, including aqueous alcoholic solutions, which unambiguously demonstrate the homolytic addition of $CH_3O\cdot$ to the substrate molecule. According to the data of Podlovchenko et al.[105], the oxidation of methanol includes several parallel stages:

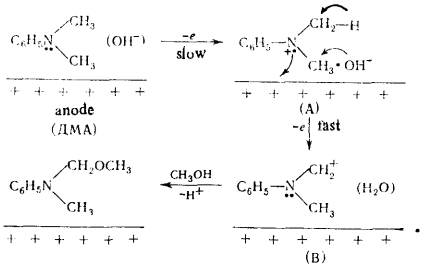
$$CH_3OH \rightarrow CH_3OH_{ads}\begin{cases}\longrightarrow SCS \rightarrow CO_2\\ \longrightarrow A_1 \rightarrow CO_2\\ \longrightarrow A_2 \rightarrow HCOOH\,(HCOO^-),\\ \longrightarrow A_3 \rightarrow H_2CO\end{cases} \qquad (19)$$

where SCS is a strongly chemisorbed substance and A_1, A_2, and A_3 are relatively weakly adsorbed species, whose composition has not been specified precisely. Analogous ideas were developed later by Breiter[106]. Although such mechanisms do not specify the nature of the adsorbed intermediates in the oxidation of the alcohol, they evidently allow a compromise with the results of electrochemical synthesis within the framework of the heterogeneous mechanism. Sasaky et al., who carried out the study on the electrochemical synthesis of alkoxybenzenes mentioned previously[52], also concluded that the reaction is heterogeneous. This conclusion is based on an analysis of kinetic data for the relation (which passes through a maximum) between the yield of the methoxy-derivative and the alcohol concentration.

In the study quoted previously[55], it was established that the products of the electrochemical synthesis of methoxy-derivatives of certain aromatic compounds differ significantly from the products of chemical methoxylation in the thermal decomposition of dimethyl peroxide (in particular, benzyl dimers, found among the products of the chemical synthesis, are not formed in the electrochemical synthesis). This anomaly can be readily explained if one postulates that the reaction layer is localised near the electrode (the high concentration of $CH_3O\cdot$ then prevents the dimerisation of benzyl radicals, promoting the formation of methoxy-derivatives).

The results of a study of the reaction involving amines lead to the conclusion that anodic alkoxylation is a heterogeneous process[17,40,73,74]. In particular, according to the data of Weinberg et al.[17,40], the adsorption of the substrate is an essential stage in the methoxylation of tertiary amines. Initially this conclusion was based on the structure of the electrochemical oxidation product of *NN*-dimethylaniline[40]. Subsequently it was confirmed by kinetic data[74]. The authors observed a fractional reaction order with respect to the amine, which is characteristic of the adsorption of substrate molecules in accordance with the Temkin or Freundlich isotherm[107]. Convincing evidence in support of the adsorption of the 1,3-diene under the conditions of anodic alkoxylation was also obtained by Zhurinov et al.[98]

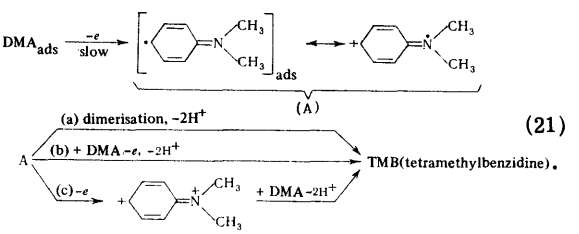
A number of studies carried out in recent years[88,103] also involved the investigation of the electrochemical behaviour of the substrate at the anode. The half-wave potentials for the oxidation of substances used in the alkoxylation reactions demonstrate the possibility, in principle, of oxidising many of them in the range potentials in which electrochemical synthesis is usually carried out. The results of studies by Eberson and coworkers[108-111] and also other workers[112-114] show that many electrochemically generated radicals may be oxidised further at their formation potentials. These data have led some investigators to hypotheses concerning the involvement of the substrate, including its ionised form, in the reaction[17,40,73,74]. For example, according to Weinberg and Reddy[17], the alkoxylation of tertiary amines proceeds via a stage involving the oxidation of the adsorbed amine molecules. Analysis of the Tafel sections of the polarisation curves and also of the potential—time relations under galvanostatic conditions led the authors to the conclusion that the molecule is oxidised electrochemically in steps. In the first, rate-limiting stage, one electron is abstracted with formation of a radical-cation. This is followed by a rapid stage with further one-electron oxidation of the radical-cation A and solvolysis with formation of the methoxy-derivative:



(20)

The wide variety of reaction products can be accounted for within the framework of this mechanism taking into account the pH of the electrolyte. The basicity of the solution promotes the deprotonation of the adsorbed radical-cation A.

In the absence of deprotonation facilitated by the hydroxide ion, the radical-cation A can enter only into the dimerisation reaction according to the equations



(21)

Kinetic data do not allow a choice between the three versions (a), (b) and (c). Other workers who investigated this reaction[74] also postulate the involvement of ionised intermediates in it, but they assume that the adsorbed radical and not the aniline molecule is oxidised. Smith and Mann[74] believe that the initial stage is the electrochemical oxidation of the methoxide anion to $CH_3O\cdot$, which dehydrogenates the amine moiety in the side chain:

$$CH_3O^- - CH_3O^\cdot + e;\ 2CH_3O^\cdot + 2PhCH_2N(CH_3)_2 \xrightarrow{-2CH_3OH} \underset{(I)}{PhCH_2-\dot{N}(CH_3)-CH_2^\cdot} + \underset{(II)}{PhCH\dot{N}(CH_3)_2}.$$

Methoxylated products are obtained as a result of the solvation of the radical-cations (III) and (IV) formed in the oxidation of the radicals (I) and (II) at the electrode:

$$\text{(I) or (II)} \xrightarrow[\text{anode}]{-e} \underset{(III)}{PhCH_2\overset{+}{N}(CH_3)-CH_2^\cdot} \text{ or } \underset{(IV)}{Ph\overset{+}{C}HN(CH_3)_2}, \qquad (22)$$

$$\text{(III) or (IV)} + CH_3O^- \rightarrow \underset{(V)}{PhCH_2N(CH_3)-CH_2OCH_3} \text{ or } \underset{(VI)}{PhCH(OCH_3)N(CH_3)_2}.$$

The preferential formation of compound (V), which was also noted by Weinberg and Reddy[17], is attributed to the higher stability of compound (II) compared with (I). The hypothesis of the electrochemical oxidation of the substrate as a necessary stage in alkoxylation has also been adopted by certain investigators for furan derivatives[22,60]. This pathway is adopted, as an alternative to the purely homolytic mechanism, for the reaction with aromatic compounds[55]. The mechanism is analogous to that discussed above and involves the oxidation at the electrode of the radical generated in the homolytic deprotonation of the substrate molecule by the electrochemically generated methoxy-radical:

$$RH \xrightarrow{CH_3O^\cdot} R^\cdot \xrightarrow[\text{anode}]{-e} R^+ \xrightarrow{CH_3O^-} ROCH_3. \qquad (23)$$

Similar views have gained acceptance for the mechanism of the formation of ethers. This process is frequently accompanied by the Kolbe reaction[67,115-119] and proceeds as follows[18]:

$$RCOO^- \xrightarrow{-e} RCOO^\cdot \xrightarrow{-CO_2} R^\cdot \xrightarrow{-e} R^+ \xrightarrow[-H^+]{CH_3OH} ROCH_3. \qquad (24)$$

Wladislaw and Viertler, who investigated the successive anodic oxidation of certain phenylacetic acids, arrived at the same conclusion. They believe that the acid molecule undergoes two-electron oxidation at the anode[119].

However, it should be noted that in many studies the formation of carbonium ions is postulated only on the basis of the formal possibility of the oxidation of substrate molecules. For a correct solution of this problem, it is necessary to carry out electrolysis in each case at a measured potential in combination with the study of the electrochemical behaviour of the substrate itself. This problem has been discussed in greater detail in two reviews[88,103].

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