# ELECTROSYNTHESES BASED ON REACTIONS OF ADDITION OF ELECTROCHEMICALLY GENERATED RADICALS TO ETHYLENE AND ITS DERIVATIVES—I. ELECTROSYNTHESIS PRODUCTS AND THE INFLUENCE OF ELECTROLYSIS CONDITIONS ON THE ADDITION PRODUCT YIELD

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Abstract—It is shown that radicals electrochemically generated under Kolbe and Brown–Walker syntheses can, in principle, be added to ethylene and its derivatives. Products formed under electrolysis of acetic, monochloroacetic, trichloroacetic, trifluoroacetic, propionic, oxalic and other acids, as well as monomethylglutarate and monomethyladipinate, in the presence of various acceptors, such as ethylene, propylene, fluoroolefins and dimethyl ester of maleic acid, are separated and identified. It is shown that products of type

$$R(-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_n R \text{ with } n = 0, 1, 2, 3 \text{ and } 4 \text{ are formed.}$$
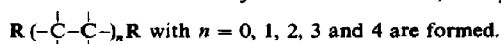
The influence of electrolysis conditions on the addition product yield is investigated. An increase in the acceptor concentration is shown to increase the total yield of addition products and the yield of higher oligomers. An increase in the current density reduces the yield of addition products.
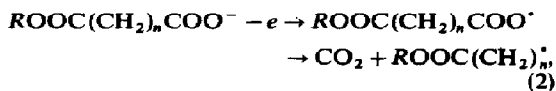
INTRODUCTION

Electrochemical methods for synthesizing organic compounds have attracted for a long time attention of researchers as effective and promising methods for obtaining many valuable organic semiproducts[1–4]. Special attention has recently been given to electrochemical dimerization processes which practically have no analogs among chemical methods. Therefore, these processes of great practical interest that resulted in the development of the corresponding industries in some countries[5–9].

Highly reactive particles, radicals and ion-radicals, can be obtained electrochemically in very high concentrations at ordinary temperatures near the electrode surface. High concentrations of reactive particles make it possible to synthesize products of interaction of these particles with one another (dimerization) and with other substances present in the reaction mixture. Such reactions can be performed electrochemically with much greater efficiency, than by conventional chemical methods.

The discharge of anions of carboxylic acids (Kolbe electrosynthesis[10])

$$RCOO^- - e \rightarrow RCOO^\cdot \rightarrow CO_2 + R^\cdot, \quad (1)$$
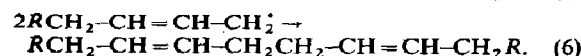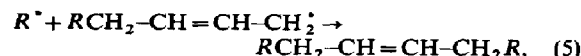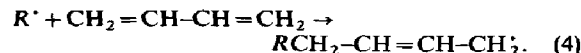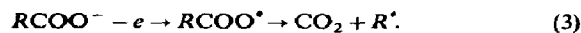
$$2R^\cdot \rightarrow R - R, \quad (1')$$

and of anions of monoesters of dicarboxylic acids (Brown–Walker reaction[11]),

$$ROOC(CH_2)_n COO^- - e \rightarrow ROOC(CH_2)_n COO^\cdot$$
$$\rightarrow CO_2 + ROOC(CH_2)_n^\cdot, \quad (2)$$

$$2ROOC(CH_2)_n^\cdot \rightarrow ROOC(CH_2)_{2n}COOR. \quad (2')$$

The mechanisms of these reactions are similar in many respects. The Brown–Walker reaction underlies a large-scale industrial electrosynthesis of sebacic acid in the USSR by electrolysis of methanol solution of monomethyl ester of adipinic acid[7–9] and electrochemical synthesis of suberic acid that has been developed lately[12]. This reaction permits one to obtain higher dicarboxylic acids with doubled number of methylene groups from low-molecular dicarboxylic acids.

Possibilities of anodic electrosynthesis were extended significantly when in 1954–1959 Lindsey and Peterson[13, 14] discovered the reaction of addition of radicals, formed under Kolbe and Brown–Walker electrosynthesis, to butadiene. This reaction was shown to proceed with dienes, *ie* compounds with conjugate double bonds[15–20] that are incorporated into a molecule of the final product, so that a double bond is always retained in final products.

$$RCOO^- - e \rightarrow RCOO^\cdot \rightarrow CO_2 + R^\cdot. \quad (3)$$

$$R^\cdot + CH_2 = CH - CH = CH_2 \rightarrow$$
$$RCH_2 - CH = CH - CH_2^\cdot. \quad (4)$$

$$R^\cdot + RCH_2 - CH = CH - CH_2^\cdot \rightarrow$$
$$RCH_2 - CH = CH - CH_2 R. \quad (5)$$

$$2RCH_2 - CH = CH - CH_2^\cdot \rightarrow$$
$$RCH_2 - CH = CH - CH_2 CH_2 - CH = CH - CH_2 R. \quad (6)$$

Methods for synthesizing unsaturated dicarboxylic acids and their esters[21–24] have been developed on the basis of this reaction.

It is known that free radicals, formed under Kolbe and Brown–Walker electrolyses, can be added to cyclohexadiene[25], pyridine[26–28], trinitrotolu-

ene[29] and styrene[30], yet those are also compounds with conjugate double bonds. At the same time, if reactions of additive dimerization could be performed with compounds with isolated double bonds (eg, ethylene), this would enable one to obtain saturated compounds from inexpensive materials, because ethylene is much cheaper than butadiene. But Kolbe electrosynthesis in the presence of ethylene has not produced products of addition of $CH_3^\cdot$ radical to ethylene[31]. It was believed, therefore, that electrochemically generated radicals can react only with compounds with activated (conjugate) double bond.

It was shown in a large series of works recently performed by the authors that electrochemically generated radicals[32–38] can be added to compounds with isolated double bond. It was shown that under electrolysis of acetates in the presence of ethylene under a pressure of 60 atm the radicals $CH_3^\cdot$ formed are added almost quantitatively to ethylene[33]. We believe that this process could not be performed earlier because of specific features of ethylene adsorption in the range of high anodic potentials where these processes of electrosynthesis take place[36].

This paper reports results for different electrosyntheses based on reactions of addition of electrochemically generated radicals to ethylene and its derivatives and also results of studying the mechanism of these reactions and the effect of electrolysis conditions on the yield of various products. The results presented refer to adsorption of ethylene on a smooth platinum electrode in the range of high anodic potentials and to the role this adsorption plays for the addition of electrochemically generated radicals.

EXPERIMENTAL

Apparatus for conducting electrosynthesis under pressure

Successful conduction of reactions of addition of electrochemically generated radicals to unsaturated acceptors largely depends on the creation of high concentrations of acceptors in the zone where the reaction takes place. Under ordinary conditions however, ethylene, propylene and fluoroolefins are very poorly soluble in electrolytes used in reactions of electrochemical synthesis. Therefore, to increase the solubility of ethylene, propylene and fluoroolefins, the process has to be conducted at elevated pressures.

To this end, we used a special stainless steel autoclave designed for a maximal pressure of 150 atm. The cup of the autoclave was provided with special connecting pipes for gas input and output, pocket for thermocouple and current leads isolated from the autoclave body with Teflon sleeves. A 100 ml electrolyser made of glass or Teflon was placed on the autoclave bottom. The electrolyser or cell could be connected according to a three-electrode scheme. Depending on experimental conditions, electrodes represented plates made of platinum, glass carbon or smooth or porous titanium promoted with platinum. In the latter case platinum was deposited on smooth or porous titanium by thermal decomposition of platinum salts at 450–550 °C, according to technique close to that described in[39]; the amount of platinum deposited was 0.1–0.4 mg cm^{-2}. The autoclave was

mounted on a magnetic agitator, with which the electrolyte was stirred.

The autoclave was connected from its one side to the system of pressurized ethylene feeding and from its other side to the gaseous products collector in the form of a comb, which permitted the extraction of samples of gaseous products under electrolysis, or in the form of a gasometer. The pressure in the autoclave was controlled by coarse and fine valves within ± 0.5 atm and was monitored by gauges. Before the electrolysis, in most cases, the solution in the autoclave was saturated for 30 min with ethylene at a given pressure. Depending on experimental conditions, other gaseous olefins were fed into the electrolyser from a vessel through a system of pipelines, or were introduced from a dosing apparatus into the autoclave, pre-evacuated (to 1 mm Hg) and cooled in liquid nitrogen, through a connecting pipe with a valve. In the latter case the autoclave was warmed up to room temperature before to switch on power supply.

Gaseous products (in the process of or after electrolysis) were released through a trap, cooled by an ice–acetone mixture, and collected in the gasometer, while volatile products of electrosynthesis or initial substances were condensed in liquid form.

Under ordinary pressure electrolyses were conducted in a special electrolyser equipped with a jacket and a reverse refrigerator.

To determine the electrolyte acidity after electrolysis, it was poured into a measuring flask and an appropriate solvent was added to increase the solution volume to a label corresponding to the initial volume. The content of free acid in the electrolyte before and after electrolysis was determined by titration of 1 ml of the electrolyte in 0.1 M aqueous solution of KOH (with the help of phenolphthalein). The degree of consumption was determined by the change in the initial and final acidity. When the acidity had been determined the electrolysis products were separated and identified. The experimental technique used permitted the determination of the amount and nature of all the electrosynthesis products, both in gaseous and liquid phase

Methods of separation, identification and quantitative analysis of electrosynthesis products

Hydrocarbon and perfluorohydrocarbon fractions of gaseous products formed in the reaction, as well as initial gaseous olefins, were analyzed by the gas–liquid chromatography technique in a column 3 m long and 3 mm in diameter with the immovable Poropak Q phase (the column temperature was 30 °C), or with a filler—aluminium oxide A-1 with 2 % squalene.

To perform qualitative analysis, we recorded the chromatogram of the gaseous electrolysis products followed by the chromatogram of individual expected products, as well as of their mixtures. The retention times for the electrolysis products were compared with the corresponding times for standard substances.

After qualitative identification quantitative analysis and calibration with respect to knowingly pure components were performed.

To separate fluoroalkylation products, the electrolyte, after determining its acidity, was diluted with a saturated aqueous solution of calcium chloride and the

organic layer was separated; the electrolysis products were three times extracted by the ester from the water fraction; the extracts were three times rinsed with water, added to the organic layer and dried above $MgSO_4$. After sublimation of the ester the residual was distillated from concentrated sulfuric acid and analyzed.

To separate dimethyl esters of higher dicarboxylic acids, the solvent was boiled down in vacuum after electrolysis, the residual was diluted with water, the products were three times extracted by the ester or methylene chloride and the extracts were three times rinsed with water and dried above $MgSO_4$. The residual, after sublimation of the ester or methylene chloride, represented a mixture of dimethyl esters of higher dicarboxylic acids that was further analyzed.

Identification and quantitative analysis of the separated products were performed by NMR[19] F, NMR[1]H, Gas–liquid chromatography (GLCh), Chromatomass-spectrometry, preparative GLCh, ir-spectroscopy and elemental analysis. NMR[19]F spectra were recorded by a Hitachi–Perkin–Elmer R-20 instrument (external CF_3COOH being the standard), and NMR[1]H spectra by a Perkin–Elmer R-12 instrument (in CCl_4; external tetramethyl silane being the standard). Mass-spectra were recorded by a Varian-Mat-CH-8 chromatomass-spectrometer (immovable phase—20% tricresyl phosphate on shimalit), GLCh was performed on a AXM-8 M D chromatograph (immovable phase—25% QF-1 on shimalit) column 4 m long and 3 mm in diameter, for the corresponding temperatures and internal standards). Preparative GLCh was performed according to the corresponding programme on a Carlo Erba instrument (immovable phase—25% QF-1 on shimalit).

RESULTS AND DISCUSSION

Addition of radicals electrochemically generated under Kolbe synthesis to ethylene and its derivatives

Ethylene. The reaction of electrolysis of acetic acid in the presence of ethylene was studied as a model system. Electrolysis was conducted at 20°C in potassium acetate solutions acidified with acetic acid. Figure 1 shows that in the absence of ethylene the only hydrocarbon product of electrosynthesis was ethane, the ordinary product of Kolbe electrosynthesis. However, when the ethylene pressure was even 5 atm, the hydrocarbon fraction contained 25% of butane and when the pressure was 60 atm the content of butane reached 67%. If solutions with an increased ethylene solubility are used (aqueous methanol, methanol, methanol–acetone), the fraction of butane in hydrocarbon gases increases (see Table 1). In the methanol–acetone solution the gas contained even 90% of butane. Thus, an increase in the concentration of the dissolved ethylene leads to an increase in the yield of the product of addition of methyl radicals to ethylene.

In liquid phase hexane was detected in the electrolysis products. Under electrolysis of the methanol solution the total composition of liquid and gaseous hydrocarbon products (under ethylene pressure 50 atm) was as follows, %: C_6H_{14}—5.3; C_4H_{10}—84.1;
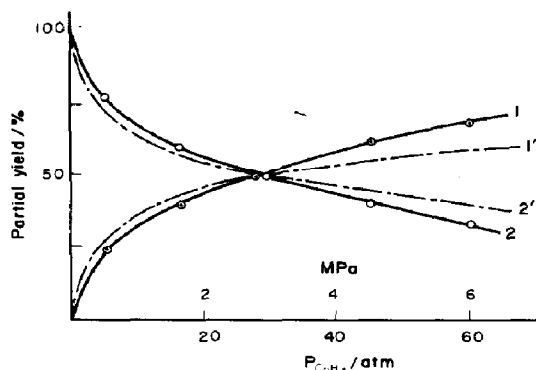

Fig. 1. Fractions of butane (1, 1') and ethane (2, 2') in anodic gases as a function of the ethylene pressure under electrolysis of aqueous solutions 3M CH_3COOK + 1 M CH_3COOH at an anodic current density of 2 mA cm^{-2}. Curves 1' and 2' are calculated from eqns. (12) and (13) of Part II for $\beta = 0.5$.

C_2H_6—10.6. The yield of these products with respect to current was 96%.

It can be seen from Fig. 2 that with an increase in the anodic current density the yield of products of addition of radicals to ethylene decreases, while the yield of the dimeric product grows (curves 1, 2). This effect is more pronounced in aqueous solutions than in aqueous alcohol ones (curves 1', 2').

Thus, we have shown, using the model system of acetate electrolysis, that reactions of electrochemical additive dimerization can proceed with the participation of ethylene under pressure.

The acetate ion, discharged on the anode, yields the methyl radical:

$$CH_3COO^- - e \rightarrow CH_3COO^{\cdot} \rightarrow CO_2 + CH_3^{\cdot}. \quad (7)$$

Methyl radicals, formed under Kolbe synthesis, can either be dimerized, yielding an ordinary product of Kolbe synthesis, ethane (for these radicals disproportionation and other processes are practically eliminated),
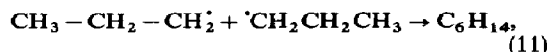
$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6, \quad (8)$$
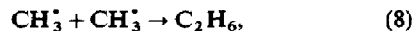
or they can interact with the ethylene molecule, yielding a new radical:

$$CH_3^{\cdot} + CH_2 = CH_2 \rightarrow CH_3 - CH_2 - CH_2^{\cdot}. \quad (9)$$

The new radical can either interact with a second methyl radical, yielding butane

$$CH_3 - CH_2 - CH_2^{\cdot} + CH_3^{\cdot} \rightarrow C_4H_{10}, \quad (10)$$
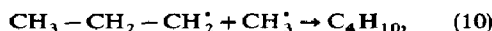
or it can be dimerized, yielding hexane

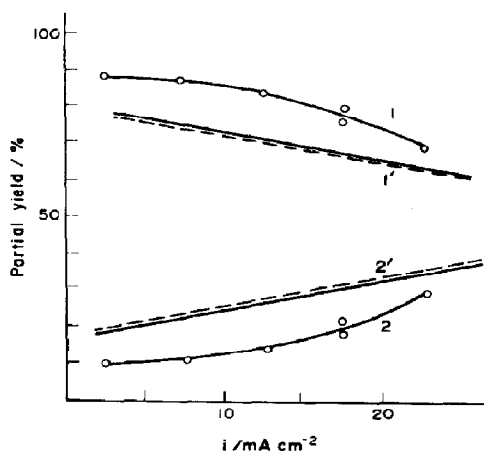$$CH_3 - CH_2 - CH_2^{\cdot} + {\cdot}CH_2CH_2CH_3 \rightarrow C_6H_{14}, \quad (11)$$

ie just the products that we discovered in the electrolysis under ethylene pressure. The situation is as if an even number of CH_2-groups is "built-in" into the molecular chain of an ordinary dimeric product.

The results have shown that under electrolysis of salts of higher-molecular monocarboxylic acids (propionic, butanoic, valerianic, *etc*) in the presence of ethylene under pressure the yield of products of addition of electrochemically generated radicals to ethylene (under the same conditions) slightly de-

Table 1. Influence of the solution composition on the yield of electrolysis products (ethylene pressure is 60 atm, current density is $2\ mA\ cm^{-2}$)
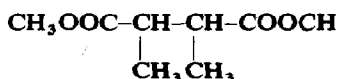
Solution (M)			Solvent (wt. %)		Hydrocarbon fraction (%)	
CH_3COOK	CH_3COOH	H_2O	CH_3OH	CH_3COCH_3	ethane	butane
3	1	100	—	—	33	67
3	1	15	85	—	20	80
0.5	3	—	100	—	15	85
0.5	3	—	50	50	10	90

Fig. 2. The effect of anodic current density on the composition of anodic gases under electrolysis of aqueous methanol (15% H_2O) (1, 2) and aqueous (1', 2') solutions 3M CH_3COOK + 1M CH_3COOH at an ethylene pressure of 60 atm: 1, 1'—ethane 2, 2'—butane. Dashed line—theory.
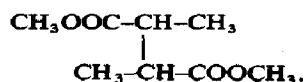
creases. On the contrary, under electrolysis of acetates in the presence of higher ethylene homologs (propylene, butenes, pentene, *etc*) the yield of the addition products increases. For instance, under electrolysis of acetates in the presence of propylene (the pressure 4–5 atm) the yield of products of addition of electrochemically-generated radicals is the same as under the ethylene pressure 60 atm.

Diesters of maleic acid. To illustrate the possibility of adding radicals, electrochemically-generated under Kolbe synthesis, to various other compounds with double bond, we have conducted electrolyses of the solution 1 M CH_3COOH + 0.5 M CH_3COOK + 1 M dimethyl ester of maleic ester in methanol on a smooth platinum electrode at a current density of 20 mA cm^{-2}.

It was found that together with a small amount of ethane (the yield, with respect to current, is ∼ 6%) the product of addition of two electrochemically-generated methyl radicals to diester of maleic acid— dimethyl ester of dimethylsuccinic acid—is formed as the main electrolysis product

$$CH_3OOC–CH–CH–COOCH$$
$$\qquad\qquad |\quad\ |$$
$$\qquad\quad CH_3\ CH_3$$

and

$$CH_3OOC–CH–CH_3$$
$$\qquad\qquad\ |$$
$$\qquad CH_3–CH–COOCH_3.$$

In this case stereoisomers are formed in approximately equal amounts.

Products of dimerization of secondary radicals were almost not formed in this case, probably due to steric difficulties. The formation of $CH_3OOCCH(CH_3)$ $CH(COOCH_3)CH(COOCH_3)CH(CH_3)COOCH_3$ was detected in trace amounts.

Similar reactions were conducted under electrolysis of propionic, butanoic, valerianic and other acids and dimethyl esters of diethylsuccinic, dipropylsuccinic and other acids were obtained and identified. The reaction proceeds with almost quantitative yield, with respect to the initial maleic acid.

It is interesting to note that if the mixture of diesters of maleic and fumaric acids is used, diester of maleic acid reacts first of all, which is an indication of sharp difference in the reactivity of stereoisomers.

Addition of radicals to acetylene. The reaction of Kolbe electrosynthesis in the presence of dissolved acetylene showed that electrochemically-generated radicals can be added to acetylene. Under electrolysis of methanol solution 1 M CH_3COOH + 0.5 M CH_3COOK at room temperature and anodic current density 20 mA cm^{-2} on platinum grid electrodes (with non-separated anodic and cathodic spaces) and in the presence of dissolved acetylene bubbling through the solution, the following products were obtained: butylene, butene, methylacetylene, as well as the products of their cathodic reduction: butane, propylene, propane. A small amount of ethane and 2,4-dimethyl-butane was also present in the electrolysis products.

Methyl radicals, electrochemically generated under Kolbe electrolysis, can be added to acetylene, yielding a new radical

$$CH_3^{\cdot} + CH \equiv CH \rightarrow CH_3–CH=CH^{\cdot}. \qquad (12)$$

The latter, on meeting the methyl radical, will produce butylene

$$CH_3–CH=CH^{\cdot} + CH_3^{\cdot} \rightarrow CH_3–CH=CH–CH_3, \qquad (13)$$
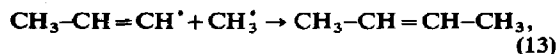
ie the product of addition of two electrochemically generated radicals to acetylene with the double bond conservation.

The product of addition of four electrochemically generated radicals to acetylene is formed only in negligible amounts:

$$4\,CH_3^{\cdot} + CH \equiv CH \rightarrow CH(CH_3)_2CH(CH_3)_2. \quad (14)$$

Under electrolysis of acetates in the presence of acetylene radicals, formed in accordance with reaction (12), disproportionate to a great extent (*cf* small yield

of dimer under electrolysis of maleic acid salts[1–3]

$$CH_3-CH=CH^\cdot + CH_3-CH=CH^\cdot \rightarrow$$
$$CH_3-C\equiv CH + CH_3-CH=CH_2 \quad (15)$$
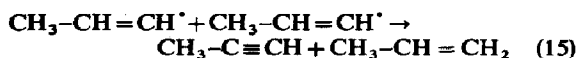
yielding propylene, methylacetylene and the product of their cathodic reduction, propane (in these experiments the cathode was also in the form of a platinum grid, so hydrogenation processes could proceed on it[40]).

Electrolysis of chloroacetic acids. Dichloroalkanes are convenient raw materials for producing diols, dinitriles and diamines, which are of interest for industrial synthesis of high-molecular compounds. That is why it was of considerable interest to study the possibility of synthesis of dichloroalkanes under electrolysis of chloroacetic acids in the presence of ethylene and its derivatives. It is known that mono-, di- and trichloroacetic acids do not form under electrolysis products typical of Kolbe electrosynthesis[1–3, 41]. At the same time, unsaturated dichlorohydrocarbons were synthesized under electrolysis of chlor-substituted carboxylic acids in the presence of butadiene[42]. For instance, under electrolysis of monochloroacetic acid in the presence of butadiene the products $ClC_6H_{10}Cl$ and $ClC_{10}H_{16}Cl$ of linear and iso-structure were obtained with the yield 20%[42].
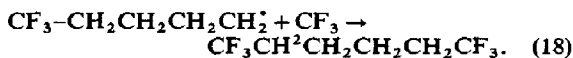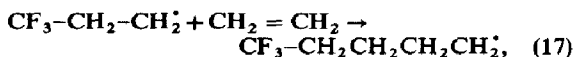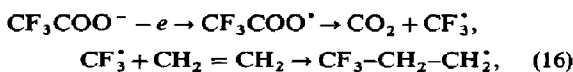
Under electrolysis of the methanol solution 0.3 M $CH_2ClCOOK + 1$ M $CH_2ClCOOH$ in the presence of ethylene under the pressure 60 atm and at the anodic current density 5–10 mA cm^{-2} the following substances were obtained: $Cl(CH_2)_4Cl$, $Cl(CH_2)_6Cl$ and $Cl(CH_2)_4OCH_3$. If acetonitrile solutions were used, the yield amounted to 70%. Thus, in this case we observed the formation of typical products of addition of electrochemically generated radicals $CH_2Cl^\cdot$ to ethylene $Cl(CH_2)_2Cl$, $Cl(CH_2)_3Cl$, $Cl(CH_2)_4Cl$, $Cl(CH_2)_6Cl$ and $ClCH_2COOCH_2Cl$, $ClCH_2COO$ $CH_2CH_2CH_2Cl$.

Under electrolysis in aqueous acetonitrile solution of trichloroacetic acid in the presence of ethylene under the pressure 60 atm the following products: $CCl_3CH_2CH_2Cl$, $CCl_3CH_2CH_2CH_2CH_2Cl$ were separated and identified in addition to ordinary products: C_2Cl_6, $CCl_3(CH_2)_2CCl_3$, $CCl_3(CH_2)_4CCl_3$. This shows that in the latter case the mechanism of the processes is much more complicated. It is interesting to note that similar products are formed in reactions of telomerization of ethylene and carbon tetrachloride[43].

Electrosynthesis of fluoroorganic compounds. We have established that under electrolysis of trifluoroacetic acid in aqueous acetonitrile (CH_3 $CN:H_2O = 8:1$) at current density 40 mA cm^{-2} and ethylene pressure 60 atm the product of addition of two radicals $CF_3^\cdot$ to two ethylene molecules—1, 1, 1, 6, 6, 6 (hexafluorohexane)—is formed with the yield, with respect to current, up to 30%. The product of addition of two radicals $CF_3^\cdot$ to one ethylene molecule was not detected.

One may assume the dimerization of olefin to be the result of the chain growth induced by free radicals $CF_3^\cdot$ formed under the discharge of anions of trifluoroacetic acid:
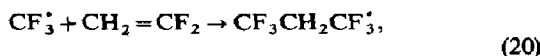
$$CF_3COO^- - e \rightarrow CF_3COO^\cdot \rightarrow CO_2 + CF_3^\cdot,$$
$$CF_3^\cdot + CH_2=CH_2 \rightarrow CF_3-CH_2-CH_2^\cdot, \quad (16)$$
$$CF_3-CH_2-CH_2^\cdot + CH_2=CH_2 \rightarrow$$
$$CF_3-CH_2CH_2CH_2CH_2^\cdot, \quad (17)$$
$$CF_3-CH_2CH_2CH_2CH_2^\cdot + CF_3 \rightarrow$$
$$CF_3CH^2CH_2CH_2CH_2CF_3. \quad (18)$$

Another reaction scheme is, however, possible, which explains the advantage of the formation of "dimeric" products, if the stage of dimerization of secondary products follows stage (16):
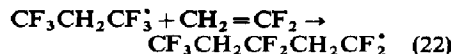
$$CF_3CH_2CH_2^\cdot + CF_3CH_2CH_2^\cdot \rightarrow$$
$$CF_3CH_2CH_2CH_2CH_2CF_3. \quad (19)$$
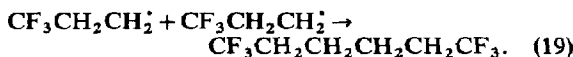
The result of electrolysis in the presence of asymmetric olefin—vinylidene fluoride (CH_2CF_2)—shows that the scheme (19) can be realized as the main direction of the reaction. The main product in this case was 2, 2, 5, 5-tetrahydroperfluorohexane in which two olefin molecules are added "head to head":

$$CF_3^\cdot + CH_2=CF_2 \rightarrow CF_3CH_2CF_2^\cdot,$$
$$(20)$$
$$2\,CF_3CH_2CF_2^\cdot \rightarrow CF_3CH_2CF_2CF_2CH_2CF_3 .(21)$$

The reason for such a high selectivity of the process is the polarization of the double bond in the vinylidene fluoride molecule. Under photochemical reaction, this fluorohydrocarbon is attacked by the electrophilic radical $CF_3^\cdot$ almost exclusively over CH_2 group[44] and by nucleophilic $CH_3^\cdot$ mainly over CF_2 group[45].

The chain growth, according to the reaction

$$CF_3CH_2CF_2^\cdot + CH_2=CF_2 \rightarrow$$
$$CF_3CH_2CF_2CH_2CF_2^\cdot \quad (22)$$

in our case encounters difficulties, probably due to the same reason: the intermediate radical $CF_3CH_2CF_2^\cdot$ is less electrophilic than $CF_3^\cdot$ and reacts slower with the olefin molecule. Therefore, the main direction of the reaction is the doubling of radicals according to reaction[(21)].

Nevertheless, the chain growth is not excluded completely; according to mass-spectroscopical and NMR^{19}F data, the product obtained contains about 5% isomeric $CF_3CH_2CF_2CH_2CF_2CF_3$.

It should be noted that the yield (with respect to substance) of products of addition of electrochemically generated trifluoromethyl radicals to vinylidene fluoride and ethylene is rather high and amounts, depending on the reaction conditions, to 60–80%, as calculated for the consumed amount of trifluoroacetic acid.

In addition to C_2H_4 and $C_2F_2H_2$, a number of fluoroolefins—3, 3, 3-trifluoropropylene ($C_3F_3H_3$), trifluoroethylene (C_2F_3H), tetrafluoroethylene (C_2F_4) and hexafluoropropylene (C_3F_6)— were used as acceptors of electrochemically generated radicals. Electrolysis of the solution of CF_3COOH/CF_3COONa in aqueous acetonitrile at current density 20–40 mA cm^{-2} and elevated pressure of $C_3F_3H_3$ produces, with the yield 42% (with respect to current), a mixture of fluorooctanes, which contains 95% of two

diastereomers $CF_3CH_2CH(CF_3)-CH(CF_3)CH_2CF_3$ and 3% of the isomeric product $CF_3CH(CF_3)$ CH_2-CH (CF_3) CH_2CF_3. In addition to the above compounds, the mixture contained traces of $(CF_3)_2CHCH_2CF_3$, ie the product of addition of two radicals CF_3^* to one $C_3F_3H_3$ molecule and 4 isomeric products of addition to three olefin molecules— $CF_3(C_3H_3F_3)_3CF_3$.

Under similar conditions C_2F_3H forms with 30% yield (with respect to current) a mixture of isomeric dihydroperfluorohexanes: $CF_3CHFCF_2CF_2CHF$ CF_3 (45%), $CF_3CHFCF_2CHFCF_2CF_3$ (50%), $CF_3CF_2CHFCHFCF_2CF_3$ (5%). Moreover, a noticeable amount of $CF_3CHFCF_2CF_3$ and traces of isomeric $CF_3(C_2F_3H)_3CF_3$ are formed in this case.

Electrolysis in the presence of C_2F_4 encounters some difficulties due to polymerization, to which this olefin is rather prone. Using current of high density, 20–60 mA cm^{-2}, we obtained with 10% yield (with respect to current) the mixture of C_4F_{10} and C_6F_{14} in the ratio 37:67; however, the main products in this case were C_2F_6 and a polymer forming a film on the anode surface.

In the reaction studied the olefin C_3F_6 is less active. Even in large excess amounts, it forms only traces of perfluoro-2-methylbutane—the product of addition of two radicals CF_3^* to one molecule. A sharp decrease in the yield of the addition product in this case agrees with the data on comparatively low activity of C_3F_6, relative to CF_3^* radicals, which amounts to 1–3% of the ethylene activity[46].

A key stage of these processes is the attack of an olefin molecule by the radical CF_3^*, which competes with rapid dimerization of these radicals. It should be noted that electrophilic radical CF_3^* attacks $C_2F_2H_2$, $C_3F_3H_3$ and C_2F_3H mainly over carbon atom enriched with hydrogen. This can be explained by the fact that polar effects play the most important role in radical reactions of fluoroolefins[44–47]. The behaviour of fluoroolefins in reactions with trifluoromethyl radicals does not depend significantly on the way of radical generation; in the anodic oxidation of trifluoroacetate ions the processes involved are similar to those observed under gas-phase and homogeneous liquid-phase reactions.

Finally, it is interesting to note that electrolysis under the same conditions, as well as in the methanol medium CH_3COOH/CH_3COONa in the presence of $C_2F_2H_2$, $C_3F_3H_3$, C_2F_3H, C_2F_4 on a platinum anode, would not result in the formation of addition products.

When conducting electrolysis (on a platinum anode) of trifluoroacetic acid in aqueous acetonitrile $(CH_3CN:H_2O = 8:1)$ in the presence of dimethyl ester of maleic acid we obtained products of addition of electrochemically generated fluoromethyl radicals to dimethyl ester of maleic acid. The main products of electrosynthesis in this case are: dimethyl ester 1, 2-bis (trifluoromethyl) of succinic acid (n_1) CH_3OOC $CH(CF_3)CH(CF_3)COOCH_3$ and dimethyl ester 1, 4-bis (trifluoromethyl)-2, 3-bis (carbomethoxy) of hexanedicarboxylic acid (n_2) $CH_3OOCH(CF_3)CH$ $(COOCH_3)CH(COOCH_3)CH(CF_3)COOCH_3$ with comparable yields. This peculiar feature enabled us to choose dimethyl ester of maleic acid as a model compound for investigating the influence of elec-

trolysis conditions on the yield of products of addition of anodically generated CF_3^*-radicals to olefins.

Figure 3 presents the yields with respect to substance (as calculated for converted trifluoroacetic acid) of dimethyl ester bis-1, 2-(trifluoromethyl) of succinic acid (n_1) and ester of tetracarboxylic acid (n_2). It can be seen from the Figure that an increase in the concentration of dimethyl ester of maleic acid in the solution leads to an increase in the total yield of the addition products. The yield of C_2F_6, ie ordinary dimeric Kolbe product, slightly decreases with the increasing concentration of dimethyl ester of maleic acid.
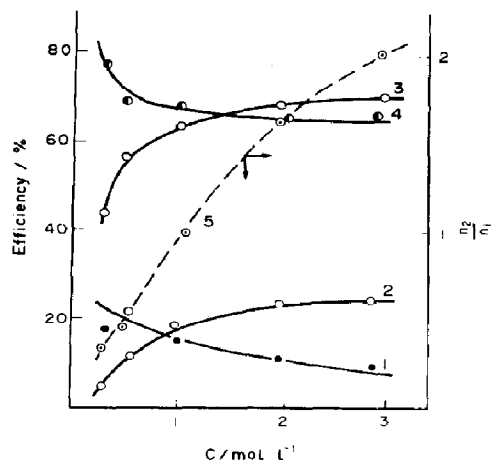

Fig. 3. The yield, with respect to substance, of products of electrolysis of 0.5 M CF_3COONa + 1.5 M CF_3COOH in aqueous acetonitrile as a function of the concentration of dimethyl ester of maleic acid at a current density of 12 mA cm^{-2}.
1—CH_3OOCCH $(CF_3)CH$ $(CF_3)COOCH_3$ (n_1);
2—$CH_3OOCCH(CF_3)-CH(COOCH_3)CH(COOCH_3)$ $CH(CF_3)COOCH_3$ (n_2); 3—$n_1 + n_2$; 4—$C_2F_6 + CF_3H$;
5—n_2/n_1.

Current density affects considerably the yield of individual products (Fig. 4). As the current density decreases, the yield of C_2F_6 drops and the yield of addition products $(n_1 + n_2)$ increases, the ratio of the products n_1 and n_2 being practically unchanged. When studying the influence of water content in the electrolyte on the yield of the main and secondary reaction products, we discovered that an increase in the water content from 1 to 50% almost does not affect the yield of products of addition of trifluoromethyl radical to the acceptor. The content of free trifluoroacetic acid in the electrolyte also influences electrosynthesis. As its content increases, the total yield of the addition products decreases.

An increase in the chain length of fluorocarboxylic acid leads, under the same other conditions, to the growth of the product of addition to one acceptor molecule in comparison with the yield of the product of addition to two acceptor molecules. Electrolysis of hexafluoroisomaleic acid leads to the formation of the product of addition of $(CF_3)_2CH^*$-radicals to one molecule of dimethyl ester of maleic acid CH_3OOC $(CH(CF_3)_2)CH-CH$ $(CH(CF_3)_2)COOCH_3$ with almost quantitative yield.
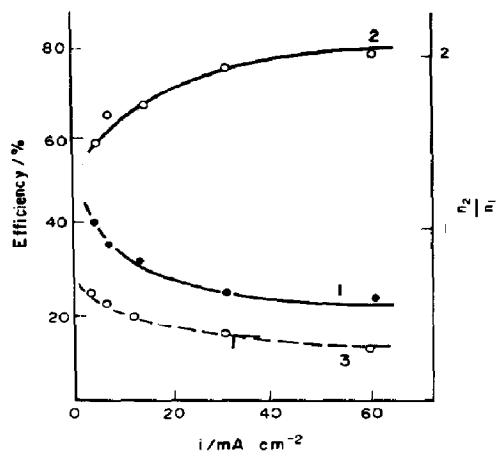
Fig. 4. Dependence of the yield, with respect to substance, of products of electrolysis of 0.5 M CF$_3$COONa + 1.5 M CF$_3$COOH in aqueous acetonitrile on the current density at the concentration of dimethyl ester of maleic acid 0.5 M. 1—n$_1$ + n$_2$; 2—C$_2$F$_6$ + CF$_3$H; 3—n$_2$/n$_1$.

Thus, electrolysis of fluorocarboxylic acids in the presence of dimethyl ester of maleic acid permits preparative synthesis of esters of dicarboxylic acids modified by fluorine.

Radicals formed under Brown–Walker reaction

Electrosynthesis of diesters of dicarboxylic acids from oxalic acid and ethylene. Oxalic acid is distinct from other dicarboxylic acids in that the dissociation constants for its first and second stages differ considerably ($K_1 = 5.36 \cdot 10^{-2}$; $K_2 = 5.42 \cdot 10^{-5}$), while for other dicarboxylic acids these constants differ by no more than one order of magnitude[48]. Therefore, oxalic acid in concentrated methanol solutions behaves almost like a strong monobasic acid and is rather easily esterified with the formation of a monoester—CH$_3$OOCCOOH; electrolysis of this monoester on a platinum anode leads to the formation of a radical CH$_3$OOC$\cdot$. Such CH$_3$OOC$\cdot$-radicals can either be dimerized, yielding an ordinary dimeric product, dimethyl ester of oxalic acid

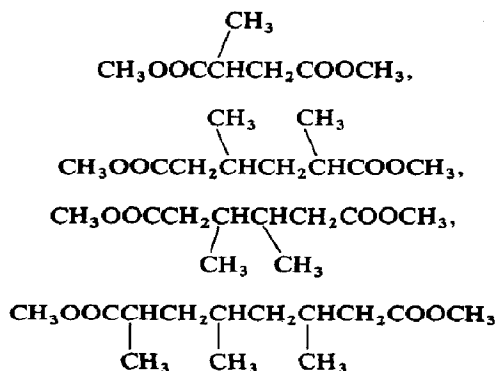$$CH_3OOC\cdot + \cdot COOCH_3 \rightarrow CH_3OOCCOOCH_3,$$
(23)
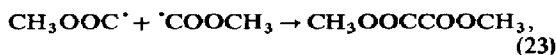
or in the presence of a radical acceptor they can react with it according to secondary radical reaction. It was shown by Fioshin *et al.*[19] that under anodic oxidation of oxalic acid on a platinum electrode in a methanol solution in the presence of 1, 3-butadiene diesters of unsaturated dicarboxylic acids are formed. However, to obtain saturated high-molecular dicarboxylic acids, widely used in polymer industry, the electrolysis products had to be hydrogenated additionally. On the contrary, the addition of carboxylic radicals, formed under electrolysis of oxalic acid, to ethylene could lead directly to the formation of diesters of saturated unbranched dicarboxylic acids. Proceeding from this fact we conducted electrolysis of methanol solution of oxalic acid in the presence of ethylene under pressure.

The analysis of the electrolysis products has shown that the separated product represents a mixture of diesters of oxalic, succinic, adipinic, suberic and sebacic acids. No other substances—secondary electrosynthesis products—were discovered. The total yield of the last four products, as calculated for the consumed amount of oxalic acid and with due account for saponification of diester of oxalic acid and its return to the cycle, ranges from 70 to 90%, depending on the process conditions. The content of each of the diesters in the mixture depends on the technological parameters.

A decrease in the ethylene pressure in the system and an increase in the current density lead to a drop of higher oligomers—dimethyl esters of suberic and sebacic. At current density 5 mA cm^{-2} and ethylene pressure 65 atm the composition of the diester mixture is as follows (%): diester of oxalic acid—29.0%, diester of succinic acid—25.0%, diester of adipinic acid—31.3%, diester of suberic acid—12.0%, diester of sebacic acid—2.7%.

An increase in the current density up to 100 mA cm^{-2} leads to a change in the mixture composition so that the content of the last two products decreases. In this case the content of diesters of oxalic, succinic, adipinic, suberic and sebacic acids in the mixture is respectively (%): 46.2; 21.3; 26.4; 5.8; 1.3.

Synthesis of branched dicarboxylic acids from ethylene homologs. Electrolysis of a methanol solution of oxalic acid on a platinum anode in the presence of ethylene homologs: propylene, butene, pentene, *etc*, leads to the formation of diesters of branched dicarboxylic acids. For instance, under electrolysis of 0.4 M methanol solution of oxalic acid in the presence of propylene under pressure 4–5 atm and at anodic current density 5 mA cm^{-2} the esters of the following branched dicarboxylic acids:

$$CH_3OOCCHCH_2COOCH_3,\ \overset{|}{C}H_3$$

$$CH_3OOCCH_2CHCH_2CHCOOCH_3,$$

$$CH_3OOCCH_2CHCH_2COOCH_3,$$

$$CH_3OOCCHCH_2CHCH_2CHCH_2COOCH_3$$

were separated and identified with a total yield (with respect to substance) of 40% with due account for the return on oxalic acid. The ratio of diesters of oxalic, methylsuccinic, dimethyladipinic and trimethylsuberic acids were 3.2:1:3.2:1.8. As the anodic current density increases, the yield of the addition products sharply decreases, especially of higher oligomers, the ratio of the diesters being 4.9:1:3:1.1 at 10 mA cm^{-2} and 8.5:1:1.7:0.47 at 50 mA cm^{-2}. To obtain higher oligomers, electrolysis of methanol solutions of oxalic acid in the presence of ethylene and its homologs has to

be conducted at low anodic current density. Electrodes with developed surface have to be used to increase effective anodic current density. Therefore, to increase the effective current density we further used anodes of porous titanium promoted with platinum. With these anodes the effective current density could be increased 5–10 fold for the same composition of the products, or the yield of higher oligomers could be increased significantly at the same low current density.

Synthesis of higher dicarboxylic acids. The development of methods for synthesizing decane dicarboxylic acid ($n = 10$), which is a semiproduct for manufacturing high-quality nylon-6, 12, has lately been of great interest. In principle, decane dicarboxylic acid might be obtained electrochemically from pimentic acid ($n = 5$) *via* Brown–Walker reaction, but pimentic acid itself is not produced now in sufficient amounts. Decane dicarboxylic acid might be obtained, in principle, *via* reaction of addition of electrochemically generated radicals to ethylene under electrolysis of monester of adipinic acid in the presence of ethylene. This would permit the production of decane dicarboxylic acid from initial materials that have been manufactured on a wide scale.

That is why in this work we have studied in detail the reaction of addition of radicals, generated under Brown–Walker electrosynthesis, to ethylene. Investigations were mainly performed with electrolysis of monomethyladipinate and monomethylglutarate under conditions maximally close to those for the production of sebacic and suberic acids.

In the electrolysis of monomethyladipinate in the presence of ethylene under pressure 1, 10-decane dicarboxylic and 1, 12-dodecane dicarboxylic acids were obtained together with sebacic acid and in the case of monomethylglutarate sebacic and 1, 10-decane dicarboxylic acids were obtained together with suberic acid. But the total yield, with respect to substance, of

the addition products did not exceed 15–17% in the first case and 20% in the second one.

It can be seen from Fig. 5 that in the absence of ethylene the ester of sebacic acid is the basic valuable electrolysis product. If ethylene is introduced, diesters of 1, 10-decane dicarboxylic and 1, 12-dodecane dicarboxylic acids are formed at $P_{C_2H_4} > 5$ atm. As the ethylene pressure grows, the yield of diesters of both 1, 10-decane dicarboxylic and 1, 12-dodecane dicarboxylic acids increases and also increases the total yield of useful diesters.

All the factors that increase the solubility of ethylene in the solution lead to the growth of the yield of diesters of higher dicarboxylic acids. If electrosynthesis is conducted in solutions with admixtures of acetone, the yield of diesters of 1, 10-decane dicarboxylic acid is 3–4% greater than in the methanol solution (Fig. 6). It can be seen from Figs. 6, 7 that anodic current density affects significantly the yield of various products. As the current density increases from 5 mA cm^{-2}, the yield of diesters of sebacic acid grows only slightly. In the presence of ethylene the yield of diesters, of 1, 10-decane dicarboxylic and 1, 12-dodecane dicarboxylic acids is maximal at 5 mA cm^{-2} and drops with the increasing anodic current density; the total yield of useful dicarboxylic acids also changes with current density.

Electrolysis of monomethyladipinate in the presence of ethylene under pressure conducted on an electrode of SU-12 glass–carbon under optimal conditions shows that though the yield of sebacic acid, as in the absence of ethylene[49], is close to that on a platinum electrode (76% in comparison with 80% on platinum), the yield of products of addition of electrochemically generated radicals to ethylene sharply decreases (only traces of 1,10-decane dicarboxylic acid are observed). Glass–carbon electrodes are not applicable to conducting reactions of additive dimerization with ethylene involved.

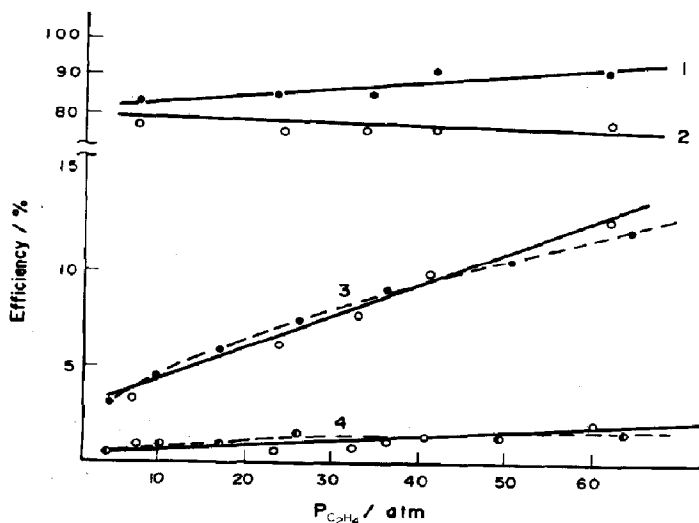In going from monomethyladipinate to monoesters

Fig. 5. The effect of ethylene pressure at $i_a = 5$ mA cm^{-2} on the yield of diesters of sebacic (2), 1, 10-decane dicarboxylic (3), 1, 12-dodecane dicarboxylic (4) acids and on the total yield of valuable diesters (1) under electrolysis of methanol solution 0.3 M $CH_3OOC(CH_2)_4COONa + 1.7$ M CH_3OOC $(CH_2)_4COOH$. Dashed lines—theory.
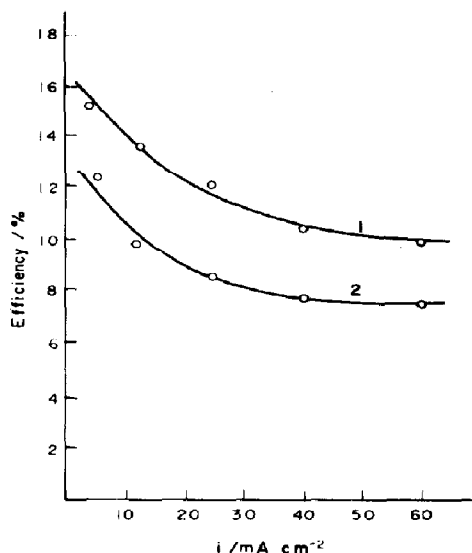
Fig. 6. The effect of anodic current density on the yield, with respect to substance, of dimethyl ester of 1,10-decane dicarboxylic acid under electrolysis of 0.3 M $CH_3OOC(CH_2)_4COONa + 1.7 M$ $CH_3OOC(CH_2)_4COOH$ in methanol–acetone (1:1) mixture (1) and methanol (2); $P_{C_2H_4} = 64$ atm.
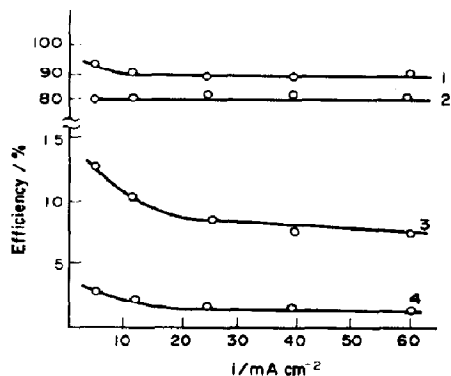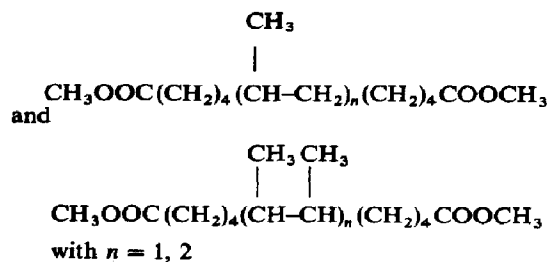

Fig. 7. The effect of anodic current density on the yield of diesters of sebacic (2), 1,10-decane dicarboxylic (3) and 1,12-dodecane dicarboxylic (4) acids and on the total yield of valuable diesters (1). Conditions as in Fig. 6.

of dicarboxylic acids with a shorter carbon chain, at the same ethylene pressure, the total yield of addition products increases, as well as a fraction of the products with the inclusion of a large number of acceptor molecules. For monomethylglutarate the yield with respect to substance is $n_1 + n_2 = 12\% + 9\%$, for succinic acid $n_1 + n_2 + n_3 = 19\% + 16\% + 8\%$, and for oxalic acid $n_1 + n_2 + n_3 + n_4 = 31\% + 40\% + 16\% + 4\%$. It is interesting to note that in this series the adsorbability of the monoester on the platinum electrode surface decreases[50]
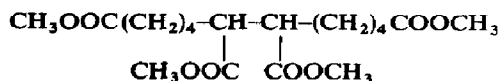
On the contrary, in going from ethylene to propylene and butene-2, under electrolysis of monomethyladipinate the yield of addition products increases and in the presence of these acceptors the results similar to those for ethylene pressure 60 atm can be

obtained even at ordinary pressure. In the presence of propylene and butene-2 the products

$$CH_3OOC(CH_2)_4 \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{(CH-CH_2)_n}(CH_2)_4COOCH_3$$

and

$$CH_3OOC(CH_2)_4 \overset{\overset{\displaystyle CH_3\ CH_3}{\displaystyle |\quad |}}{(CH-CH)_n}(CH_2)_4COOCH_3$$

with $n = 1, 2$

were separated and identified.

The analysis performed after electrolysis of a methanol solution of monomethyladipinate in the presence of 1M dimethyl ester of maleic acid shows that tetraester of tetracarboxylic acid

$$CH_3OOC(CH_2)_4 \overset{\overset{\displaystyle \ \ \ |\quad\ \ |}{\displaystyle -CH-CH-}}{\underset{\underset{\displaystyle CH_3OOC\quad COOCH_3}{\displaystyle |\qquad\ |}}{}}(CH_2)_4COOCH_3$$

is formed in addition to diethyl ester of sebacic acid.

Together with the ester of 1, 5, 6, 10-decane tetracarboxylic acid Bogoslovsky and Mirkind[51] observed in this reaction the formation of the ester of 1, 5, 6, 7, 8, 12-dodecane hexacarboxylic acid, ie the inclusion of two molecules of the diester of maleic acid into the product. The authors believe that the efficiency attained under optimal conditions (yield, with respect to substance, of the esters—90%, of the addition products—50%) permits this reaction to be considered a promising method for producing tetra- and hexacarboxylic acids, which are valuable monomers for synthetic resins with special properties.

The above authors have recently performed[51] the addition of radicals, electrochemically generated under electrolysis of monomethyladipinate, to unsaturated alcohols: allyl alcohol, 2-propyn-1-ol, 2-butyne-1, 4-diol, as well as to alcohols of alkyne series and have shown the possibility of direct synthesis of oxiesters. In the case of allyl alcohol, dimethyl ester of 5-oximethylene-1, 10-decane dicarboxylic acid

$$CH_3OOC(CH_2)_4 \overset{\overset{\displaystyle }{\displaystyle }}{CH-CH_2}(CH_2)_4COOCH_3$$
$$|$$
$$OH$$
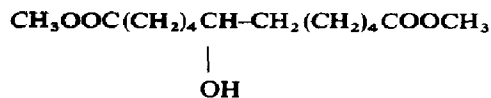
was separated and identified.

We have also performed electrolyses of monomethyladipinate in the presence of tetrachlorethylene ($CCl_2 = CCl_2$), but the products of fixation of electrochemically generated radicals by tetrachlorethylene have not been discovered.

REFERENCES

1. C. J. Brockman, *Electro-organic Chemistry*, New York (1926).
2. F. Fichter, *Organische Electrochemie*, Dresden (1942).
3. M. J. Allen, *Organic Electrode Processes*, p. 95, Reinhold, New York (1958).
4. M. M. Baizer, *Organic Electrochemistry*, Marcel Dekker, New York (1973).
5. J. Prescott, *Chem. Engng* 72, 238 (1965); *Nitrogen*, No. 26, 35 (1965).

6. *Chem. Engng News*, **45**, 58 (1967).
7. G. N. Freidlin, A. P. Tomilov and V. D. Bezuglyi, in *Progress in Electrochemistry of Organic Compounds. Electrosynthesis and Mechanism of Organic Compounds*, p. 122, Nauka, Moscow (1973) (in Russian).
8. G. N. Freidlin, E. P. Kovsman, A. A. Adamov, E. A. Pavlov, M. S. Timagina and V. I. Shevchenko, in *News of Electrochemistry of Organic Compounds*, Tula, 1976 (abstracts); p. 4 Nauka, Moscow (1976) (in Russian).
9. G. N. Freidlin, E. P. Kovsman, A. A. Adamov, M. S. Timagina and V. I. Shevchenko, in *Electrosynthesis of Monomers*, pp. 28, 49, Nauka, Moscow (1980) (in Russian).
10. H. Kolbe, *Annls Chim.*, **69**, 279 (1849).
11. A. Brown and J. Walker, *Annls. chim.* **261**, 115 (1891).
12. G. A. Tarkhanov, L. I. Solovyova, E. P. Kovsman and G. N. Freidlin, *Elektrokhimiya* 7, 288 (1971); E. P. Kovsman, S. S. Gluzman, G. A. Tarkhanov, N. I. Faingol'd, G. N. Freidlin and T. F. Samoshina, *Elektrokhimiya* **10**, 543 (1974).
13. U. S. Patent, 2.680.713 (1954); C. A., **48**, 9847 (1954).
14. R. Lindsey and M. Peterson, *J. Am. chem. Soc.* **81**, 2073 (1959).
15. W. Smith and H. Gilde, *J. Am. chem. Soc.* **81**, 5325 (1959).
16. W. Smith and H. Gilde, *J. Am. chem. Soc.* **82**, 659 (1960).
17. M. Ya. Fioshin, *Neftekhimiya* **2**, 557 (1962).
18. L. A. Mirkind and M. Ya. Fioshin, *Zh. fiz. khim.* **38**, 2223 (1964).
19. M. Ya. Fioshin, L. A. Mirkind, L. A. Salmin' and A. G. Kornienko, *Zh. vses. khim. Obshch.* **10**, 238 (1965).
20. M. Ya. Fioshin, A. I. Kamneva, L. A. Mirkind and L. A. Salmin', *Dokl. Akad. Nauk. SSSR* **138**, 173 (1961).
21. A. G. Kornienko, A. V. Uvarov, L., A. Mirkind and M. Ya. Fioshin, *Elektrokhimiya* 4, 1147 (1978).
22. M. Ya. Fioshin, A. I. Kamneva, L. A. Kornienko and L. A. Salmin', *Khimicheskaya promyshlennost'* 804 (1966).
23. A. G. Kornienko, L. A. Mirkind and M. Ya. Fioshin, *Elektrokhimiya* 5, 1003 (1969); 6, 1592 (1970).
24. M. Ya Fioshin, L. A. Mirkind and A. G. Kornienko, *Zh. veses. khim. Obshch.* **19**, 600 (1974).
25. W. Smith and H. Gilde, *J. Am. chem. Soc.* **83**, 1355 (1961).
26. S. Goldschmidt, *Angew. Chem.* **69**, 132 (1957).
27. F. Fichter and H. Stenzl, *Helv. chim. Acta* **22**, 970 (1939).
28. FRG Patent 952807, 1956, *Chem. Abstr.* **53**, 16160(1959).
29. L. Fieser, R. Clapp and W. Daubt, *J. Am. chem. Soc.* **64**, 2052 (1942).
30. S. Goldschmidt and E. Stockl, *Ber.* **85**, 630 (1952).
31. R. Renaud and D. Sullivan, *Can. J. Chem.* **51**, 772 (1973).
32. K. G. Karapetian, A. A. Bezzubov, L. S. Kanevsky, A. M. Skundin and Yu. B. Vasiliev, *Elektrokhimiya* **12**, 1622, 1623 (1976).
33. K. G. Karapetian, L. S. Kanevsky, A. M. Skundin, Yu. B. Vasiliev, E. P. Kovsman and G. N. Freidlin, *Elektrokhimiya* **12**, 662 (1976).
34. K. G. Karapetian, I. V. Proskurovskaya, A. A. Bezzubov, L. S. Kanevsky, A. M. Skundin and Yu. B. Vasiliev, *Elektrokhimiya* **13**, 544 (1977).
35. Yu. B. Vasiliev, L. S. Kanevsky, K. G. Karapetian, E. P. Kovsman, A. M. Skundin, G. A. Tarkhanov and G. N. Freidlin, *Elektrokhimiya* **14**, 770 (1978).
36. K. G. Karapetian, S. I. Andruseva, E. P. Kovsman, O. A. Khazova, L. S. Kanevsky and Yu. B. Vasiliev, *Elektrokhimiya* **15**, 487 (1979).
37. V. A. Grinberg, V. R. Polishchyuk, E. I. Mysov, L. S. German, L. S. Kanevsky, V. V. Tsodikov and Yu. B. Vasiliev, *Izv. AN SSSR ser. Khim.*, No. 12, 2825 (1977).
38. V. A. Grinberg, V. R. Polishchyuk, L. S. German, L. S. Kanevsky and Yu. B. Vasiliev, *Izv. AN SSSR ser. Khim.*, No. 3, 673 (1978) No. 5, 1056 (1979).
39. C. Iwakura, K. Fukuda and H. Tamura, *Electrochim. Acta*, **21**, 501 (1976).
40. Yu. B. Vassiliev, V. S. Bagotzky, O. A. Khazova, V. V. Cherny and A. M. Meretsky, *J. electroanal. Chem.* **98**, 253, 273 (1979).
41. F. Pattison, J. Stotcher and R. Wolford, *J. Am. chem. Soc.* **78**, 2255 (1956).
42. M. A. Khrizolitova, L. A. Mirkind and M. Ya. Fioshin, *Dokl. Akad. Nauk. SSSR*, **182**, 617 (1968); *Trudy, mosk. Khim.–tekhnol. Inst.* No 58, 164 (1968); *Zh. Org. Khimii* **6**, 219 (1970); *Elektrokhimiya* **5**, 1018 (1969) *Zh. vses. khim. Obsch.* **15**, 230 (1970).
43. R. M. Joyce, W. E. Hanford and J. Harman, *J. Am. chem. Soc.* **70**, 2529 (1948).
44. G. L. Fleming, R. M. Haszeldine and A. E. Tipping, *J. chem. Soc. Perkin Trans.* I, 574 (1973).
45. J. M. Tedder, J. C. Walton and K. D. R. Winton, *J. chem. Soc., Faraday Trans.*, I, **68**, 1806 (1972).
46. H. C. Low, J. M. Tedder and J. C. Walton, *J. chem. Soc., Faraday Trans.* I, **72**, 1300 (1976).
47. J. H. Cape, A. G. Greig, J. M. Tedder and J. C. Walton, *J. chem. Soc., Faraday Trans.* I, **71**, 592 (1975).
48. *A Concise Reference Book of Physical and Chemical Quantities*, p. 114, Khimiya, Leningrad (1967) (in Russian).
49. L. S. Kanevsky, Yu. B. Vasiliev, N. T. Presnova and E. P. Kovsman, *Elektrokhimiya* **12**, 274, 783, 1487 (1976); **13**, 440 (1977).
50. S. J. Andrusjova, E. P. Kovsman and Yu. B. Vasiliev, *Elektrokhimiya* **16**, 1231 (1981).
51. K. G. Bogoslovsky and L. A. Mirkind, in *News of the Electrochemistry of Organic Compounds* 1980, pp. 122, 123 Novocherkassk (1980) (in Russian); *Dokl. Akad. Nauk, SSSR*, **254**, 123 (1980).