Electrochemical reduction of CO_2 in the presence of 1,3-butadiene using a hydrogen anode in a nonaqueous medium

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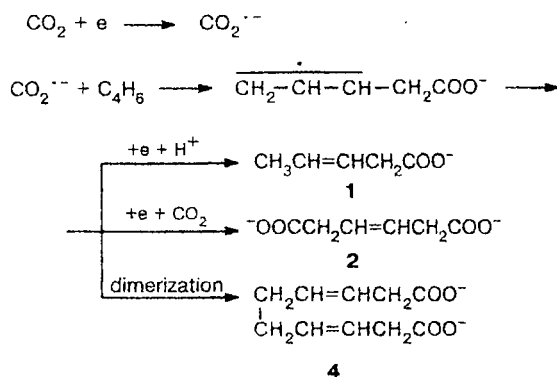*Wilmington, DE 19880-0262, USA.*
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The possibility of anodic generation of a solvated proton on a gas-diffusion electrode in an aprotic medium in the presence of carbon dioxide and 1,3-butadiene has been demonstrated. Formic acid was shown to be the only product of the reaction in the initially aprotic medium with the use of a hydrogen gas-diffusion anode. The influence of the counterion on the reactivity of the $CO_2 \cdot{}^-$ radical anion in electrocarboxylation was shown experimentally.

Key words: electrocarboxylation of butadiene, hydrogen gas-diffusion anode.

During the last thirty years, intensive studies aimed at the synthesis of adipic acid based on butadiene have been carried out. Prominent amongst these are those dealing with electrochemical carboxylation of butadiene. Electrocarboxylation of butadiene and other conjugated dienes has been described previously;[1—6] however, the reaction mechanism is still unknown.

Most probably, the process starts with cathodic reduction of CO_2 and addition of the $CO_2 \cdot{}^-$ radical anion to butadiene:[7]

$$CO_2 + e \longrightarrow CO_2 \cdot{}^-$$

$$CO_2 \cdot{}^- + C_4H_6 \longrightarrow \overset{\bullet}{CH_2}-CH-CH-CH_2COO^- \longrightarrow$$

$$\begin{array}{l} \xrightarrow{+e + H^+} CH_3CH=CHCH_2COO^- \\ \qquad\qquad\qquad \textbf{1} \\ \xrightarrow{+e + CO_2} {}^-OOCCH_2CH=CHCH_2COO^- \\ \qquad\qquad\qquad \textbf{2} \\ \xrightarrow{dimerization} \begin{array}{l} CH_2CH=CHCH_2COO^- \\ | \\ CH_2CH=CHCH_2COO^- \end{array} \\ \qquad\qquad\qquad \textbf{4} \end{array}$$

The initial electroreduction of CO_2 is confirmed by the voltammetry data for various electrode materials.[1,7]

However, some researchers believe that the formation of carboxylic or dicarboxylic acids under the conditions of butadiene electrocarboxylation follows a nucleophilic mechanism and involves the allylic anion, formed initially upon the reduction of butadiene. No voltammetric data that would support this viewpoint

have been reported.[2,6] However, it can be considered to be known with certainty that, in both cases, the arising intermediate species react at the cathode surface[8] and that the yield of the electrocarboxylation products formed from butadiene depends appreciably on the electrode material;[3,8] this apparently indicates the electrocatalytic nature of the reaction.

The choice of the anode reaction is among the most complicated problems in the electrocarboxylation of butadiene. Several variants of this reaction have been reported:

(1) generation of a hydrated proton in the anode compartment of the cell by electrooxidaton of water, and its diffusion through an ion-exchange membrane into the compartment containing an aprotic catholyte;[3,7]

(2) electrooxidation of a supporting electrolyte in a nonaqueous medium with the generation of tetraalkylammonium cations;[1,2,4,8]

(3) electrooxidation of an anode material with the generation of metal ions (see, for example, Ref. 9).

Analysis of the published data on the electrocarboxylation of butadiene and other olefins[1—11] and on the electroreduction of CO_2 in various media[12—17] reveals the following features: the $CO_2 \cdot{}^-$ radical anion acts as a C-centered radical to give C-carboxylation products only when metal or ammonium cations serve as the counterions. When a proton is the counterion, formic acid is the only reaction product. Obviously, these results are at variance with the data,[3,7] according to which cathodic carboxylation of butadiene in acetonitrile containing 0.1—1.0% water with proton generation in the anode compartment of the cell gave 3-pentenoic and 3,7-decadienedioic acids (together with formic acid)

and the addition of a dehydrating agent (MgO) to a catholyte resulted in hexenedioic acid being formed apart from the above-mentioned products.

The possibility of using the proton as the counterion in the synthesis of carboxylic and dicarboxylic acids from CO_2 and butadiene is of considerable interest because this would open up the way for the preparation of free acids rather than their salts. However, our attempts to reproduce the results on the electro-carboxylation of butadiene in a diaphragm process (with water oxidation as the anodic reaction)[3,7] gave formic acid as the only reaction product. The researchers cited[3,7] pointed out that the product composition depends substantially on the water content in the catholyte without discussing the mechanism of this dependence. In the present work, we studied the cathodic carboxylation of butadiene with proton as the counterion under strictly anhydrous conditions (oxidation of dihydrogen with generation of a solvated proton served as the anodic reaction[18,19]); thus, the formation of products due to the presence of water in the electrolyte was ruled out.
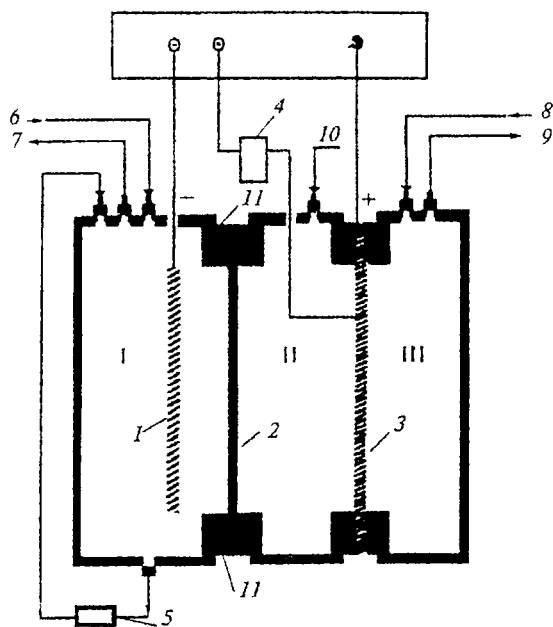
Fig. 1. The scheme of a flow cell with a gas-diffusion hydrogen anode: I, cathode compartment; II, anode compartment with liquid electrolyte; III, anode gas compartment; *1*, cathode; *2*, the Nafion-117 ion-exchange membrane; *3*, hydrogen gas-diffusion anode; *4*, reference electrode (s.c.e); *5*, centrifugal pump; *6*, *7*, branch pipes for the inlet and outlet of CO_2 and 1,3-butadiene; *8*, *9*, branch pipes for the inlet and outlet of hydrogen; *10*, branch pipes for the introduction of the anolyte; *11*, rubber gaskets. (Points II, *2*, and *10* were used only for the preparative-scale electrolysis with an aqueous anolyte.)

Experimental

The cell and electrodes. To study hydrogen gas-diffusion electrodes (GDE) with a working surface area of 7 cm^2, they were placed in the cell shown schematically in Fig. 1. The cell consists of liquid (I) and gas (III) compartments; it is also possible to mount additionally the third liquid compartment (II), which can be separated by a membrane. GDE was hermetically fastened between two ring rubber gaskets. Prior to the measurements in aprotic solvents, GDE was subjected to anodic polarization in 5 *N* KOH in order to restore its activity; then it was washed with distilled water, and dried *in vacuo* at 90 °C. Hydrogen was supplied from the side of the hydrophobic layer of GDE at a slight excess pressure. Hydrogen was dried by passing through a strong sulfuric acid.

Study of the activity of gas-diffusion electrodes in aqueous solutions of sulfuric acid and sodium hydroxide demonstrated that they surpass in their characteristics the gas-diffusion electrodes described previously.[19] Thus at a potential of 900 mV *vs* a saturated calomel electrode in 0.1 *M* KOH, the current density of hydrogen ionization was 150 mA cm^{-2}, which is 3 times higher than the current density of hydrogen ionization attained previously under the same conditions.[19]

Lead, tin, stainless steel, and glass carbon were used as cathodic materials. In some experiments in which the cathode and anode compartments were separated by a membrane, an amalgamated lead electrode was used.

Voltammetric measurements and preparative-scale electrolysis were carried out in a three-electrode circuit using an aqueous saturated calomel electrode (s.c.e.) as the reference electrode. Prior to the measurements, the electrolyte was purged with dry argon or with preliminarily dried CO_2 and 1,3-butadiene. 1,3-Butadiene was dried by molecular sieves and solid alkali and CO_2 was passed through a vessel with a strong H_2SO_4.

Preparative-scale electrolysis was carried out with the electrolyte circulating at a flow rate of 1000 cm^3 min^{-1} through the cathodic compartment equipped additionally with a reflux condenser and a bubbler.

Acetonitrile (AN) and DMF, used for the preparative-scale electrolysis and voltammetric measurements, were dried by standard procedures. The salts $(C_4H_9)_4NClO_4$ and $(C_4H_9)_4NBF_4$ were prepared from the corresponding acids and $(C_4H_9)_4NOH$ and reprecipitated with ether from EtOH. All salts were dried over P_2O_5 and stored in a dry box under argon.

Voltammograms were recorded on a PI-50.1 potentiostat using an H-308 XY-recorder. The charge was determined by integrating the corresponding I—τ curves.

The electrolysis products were analyzed by GLC (10% FS-1265 on Chromosorb, 160 °C, dimethyl oxalate as the internal standard) and by GC/MS on a V-6-7070 mass spectrometer (ionization energy 70 eV, OV+SE as the stationary phase, 30—220 °C, 2.5 °C min^{-1}).

Gas-diffusion electrodes. Three types of GDE were used; each of them had a hydrophobic layer (HL) to prevent the catalytic layer from getting wet with the liquid phase, an active catalytic layer (CL), and a current supply.

(*A*) *electrodes of the first type.* The HL was made of disperse Teflon that had been subjected to heat pretreatment; the CL was disperse platinum (20—30 mg cm^{-2}) mixed with Teflon (5 mg cm^{-2}); and a platinum or nickel gauze served as the current collector;

(*B*) *electrodes of the second type.* The HL was made of Teflon with acetylene black (AD-100); the CL was a mixture of hydrophobized acetylene black (33% w/w) and a catalyst

(tungsten carbide WC, 210 mg cm^{-2}, or Pt : Pd = 1 : 1, 4.53 mg cm^{-2}), and the current supply was a nickel gauze;

(*C*) *electrodes of the third type.* The HL was the same as in type (*B*); the CL was a mixture of disperse Pt and Pd (1 : 1) (36 mg cm^{-2}) and a 6% suspension of Teflon (0.5 ml); and the current supply was a platinum gauze.

The GDE of types *A* and *C* were produced by cold pressing ($p = 250—300$ kg cm^{-2}) followed by annealing at 340 °C under a pressure of 0.1 kg cm^{-2}.

A typical experiment with a hydrogen anode. Electrocarboxylation of 1,3-butadiene was carried out in a diaphragmless cell with various cathode catalysts (Pb, Sn, stainless steel, glass carbon, amalgamated lead) in anhydrous AN or DMF with 0.1 *M* Bu$_4$NBF$_4$ as the supporting electrolyte and with a hydrogen gas-diffusion platinum or platinum-palladium electrode as the anode. The electroreduction of CO$_2$ in the presence of butadiene was carried out at cathodic current density of 1—10 mA cm^{-2} with a controlled hydrogen anode potential. The potential of the polarized anode did not exceed 0.3—0.8 V *vs* s.c.e. This anodic potential is smaller than the potentials at which the target products of electrolysis start to oxidize.[8] The electrolyte saturated with a mixture of CO$_2$ and butadiene was passed through the cell at a flow rate of 1000 cm^3 min^{-1}. The charge varied from 0.003 to 0.078 F.

Examples of electrosynthesis. *Entry 1.* AN (50 mL) and (C$_4$H$_9$)$_4$NClO$_4$ (1.6 g, 0.01 mol) was placed in a diaphragmless electrochemical cell with a Pb cathode ($S = 3$ cm^2) and a platinum hydrogen gas-diffusion anode ($S = 7$ cm^2). The pressure of hydrogen was 100 mm H$_2$O. 1,3-Butadiene (0.07 mol, 1.57 L) was passed from a gas meter through a drying agent into the working solution for 30 min. Carbon dioxide was bubbled through the electrolyte at a rate of 15 mL min^{-1}. The electrolyte was passed through the cell at a rate of 1000 cm^3 min^{-1}. The galvanostatic electrolysis was carried out at a cathodic current density of 10 mA cm^{-2} ($I = 30$ mA) and a temperature of 20 °C. After 756 C (0.0078 F per 7 h) had been passed, the electrolysis was terminated, the reaction mixture was neutralized by aqueous K$_2$CO$_3$ to pH 9 and concentrated on a rotary evaporator, and the solid residue was dissolved in dilute H$_2$SO$_4$ (15%) and extracted with ether (3×40 mL). After evaporation of the ether, the residue was treated with diazomethane in ether until the N$_2$ evolution ceased. The products were analyzed by GLC and GC/MS. Only traces of methyl formate were detected.

Entry 2. Dry MgO (200 mg) was added to the electrolyte; all other conditions of electrolysis were identical to those used in entry *1*. After evaporation of the ether, the residue (70 mg) was treated with diazomethane in ether until N$_2$ evolution ceased. The products were analyzed by GLC and GC/MS. The following compounds were identified: methyl 3-pentenoate (**1**) (two isomers), *m/z* (I_{rel} (%)): 114 [M]$^+$ (35); 99 [M − CH$_3$]$^+$ (3); 83 [M − CH$_3$O]$^+$ (10); 82 [M − CH$_4$O]$^+$ (10); 72 [C$_3$H$_4$O$_2$]$^+$ (12); 59 [MeOCO]$^+$ (33); 55 [CH$_2$CH=CHCH$_2$]$^+$ (10); 54 [CH$_2$CH=CHCH$_2$]$^+$ (13); 53 [C$_4$H$_5$]$^+$ (10); 39 [C$_3$H$_3$]$^+$ (15); 29 [COH]$^+$ or [C$_2$H$_5$]$^+$ (28); 27 [C$_2$H$_3$]$^+$ (21); 15 [CH$_3$]$^+$ (20); dimethyl 3-hexenedioate (**2**) *m/z* (I_{rel} (%)): 172 [M]$^+$ (3); 141 [M − CH$_3$O]$^+$ (30); 140 [C$_7$H$_8$O$_3$]$^+$ (38); 113 [C$_6$H$_9$O$_2$]$^+$ (50); 112 [C$_6$H$_8$O$_2$]$^+$ (30); 99 [C$_5$H$_7$O$_2$]$^+$ (30); 81 [C$_5$H$_5$O]$^+$ (15); 82 [C$_5$H$_6$O]$^+$ (7); 71 [C$_3$H$_4$O$_2$]$^+$ (100); 59 [CO$_2$Me]$^+$ (85); 55 [C$_4$H$_7$]$^+$ (11); 53 [C$_4$H$_6$]$^+$ (25); 41 [C$_3$H$_5$]$^+$ (35); 39 [C$_3$H$_3$]$^+$ (20); 29 [HCO]$^+$ or [C$_2$H$_5$]$^+$ (25); 28 [CO]$^+$ or [C$_2$H$_4$]$^+$ (7); 27 [C$_2$H$_3$]$^+$ (23); 15 [CH$_3$]$^+$ (70).

According to GLC, the contents of esters **1** and **2** in the residue obtained after treatment with diazomethane was 65%;

the ratio **1** : **2** = 3 : 1. The total current yield of esters **1** and **2** was 3.7%. No dimethyl 3,7-decadienedioate was detected.

Entry 3. Electrocarboxylation was carried out in a cell with separated cathode and anode compartments equipped with a Nafion-117 membrane in the NH$_4^+$ form. As the cathode, SU-2000 glass carbon ($S = 12$ cm^2) was used; and a hydrogen gas-diffusion electrode ($S = 7$ cm^2) was used as the anode. The pressure of hydrogen was 100 mm H$_2$O. The catholyte composition was as follows: DMF (50 mL), Bu$_4$NBF$_4$ (0.6 g, 0.0018 mol), and isoprene (0.544 g, 0.008 mol). The anolyte composition was as follows: NH$_3$ (7.5 g, 0.44 mol), NH$_4$BF$_4$ (1.5 g, 0.014 mol), and 50 mL of H$_2$O. Carbon dioxide was bubbled through the catholyte at a velocity of 15 mL min^{-1}. The catholyte was pumped at a flow rate of 1000 cm^3 min^{-1}. The electrolyte was subjected to galvanostatic electrolysis at a cathodic current density of 10 mA cm^{-2} ($I = 125$ mA) and a temperature of 20 °C. After passing 2233 C (0.023 F over a period of 5 h), the electrolysis was stopped, and the catholyte was treated as in entry *1* to give 100 mg of a mixture of reaction products, which contained, according to GLC and GC/MS, 50% of methyl 4-methyl-3-pentenoate (one isomer) Me$_2$C=CH−CH$_2$−COOMe (**3**) *m/z* (I_{rel} (%)): 127 [M − H]$^+$ (2); 113 [M − CH$_3$]$^+$ (25); 98 [M − C$_2$H$_6$]$^+$ (7); 84 [C$_4$H$_4$O$_2$]$^+$ (15); 69 [C$_5$H$_9$]$^+$ (12); 66 [C$_5$H$_6$]$^+$ (12); 58 [C$_2$H$_2$O$_2$]$^+$ (40); 43 [C$_2$H$_3$]$^+$ (100); 27 [C$_2$H$_3$] (18); 15 [CH$_3$]$^+$ (8). No methyl C(7)-alkenedioates or C(12)-dodecadienoates were detected. Methyl formate was also found among the electrolysis products. The current yield of methyl 4-methyl-3-pentenoate was 3.5%.

Entry 4. Electrocarboxylation was carried out in a cell with separated cathode and anode compartments, equipped with a Nafion-117 membrane in the H$^+$-form. Lead ($S = 15$ cm^2) was used as the cathode, and a hydrogen gas-diffusion electrode ($S = 7$ cm^2) was used as the anode. The hydrogen pressure was 100 mm H$_2$O. The catholyte contained DMF (50 mL), Bu$_4$NBF$_4$ (1.5 g, 0.0045 mol), and Et$_3$N (10 g, 0.099 mol). Dried butadiene (3 g, 0.055 mol) was passed through a catholyte for 30 min, and carbon dioxide was bubbled through the catholyte at a rate of 15 mL min^{-1}. The catholyte was passed at a flow rate of 1000 cm^3 min^{-1}. The anolyte was 1% H$_2$SO$_4$. Galvanostatic electrolysis was carried out at a cathodic current density of 10 mA cm^{-2} ($I = 150$ mA) and a temperature of 20 °C. After passing 2991 C (0.031 F over a period of 6 h), the electrolysis was stopped, and the electrolyte was treated as in entry *1* to give 100 mg of a product mixture containing, according to GLC and GC/MS, methyl 3-pentenoate (**1**) (two isomers), dimethyl hexenedioate (**2**) (three isomers), dimethyl 3,7-decadienedioate (**4**) (two isomers), and dimethyl oxalate. The total current yield of products (**1**, **2**, **4**) was 3.4%.

Entry 5. Electrocarboxylation of butadiene was carried out in a 150-mL diaphragmless Teflon cell placed in a stainless-steel autoclave. A mixture of Bu$_4$NBF$_4$ (2.2 g, 0.006 mol), dry NH$_3$ (1.5 g, 0.088 mol), and 1,3-butadiene (3 g, 0.055 mol) in 100 mL of MeCN was subjected to galvanostatic electrolysis using a lead cathode ($S = 25$ cm^2) and a platinum anode ($S = 20$ cm^2) at a CO$_2$ pressure of 3.2 atm, a cathode current density of 10 mA cm^{-2} ($I = 250$ mA), and a temperature of 20 °C with stirring with a magnetic stirrer. After passing 1800 C (0.018 F over a period of 5 h), the electrolysis was stopped, and the electrolyte was treated as in entry *1* to give 100 mg of a liquid mixture of reaction products, which contained, according to GLC and GC/MS, methyl 3-pentenoate (**1**) (two isomers), dimethyl 3-hexenedioate (**2**) (two isomers), dimethyl 3,7-decadienedioate (**4**) (two isomers), and dimethyl oxalate.

The 1 : 2 : 4 ratio was 2.5 : 4 : 1. The reaction products were also found to contain $NCCH_2COOMe$, m/z (I_{rel} (%)): 99 $[M]^+$ (2); 59 $[MeOCO]^+$ (100); 40 $[C_2H_2N]^+$ (30); 15 $[CH_3]^+$ (60), indicating that CO_2 can react with the solvent, and a loose white precipitate, which was apparently ammonium carbamate $[N_2NCOO][NH_4]$; the formation of ammonium carbamate on passing dry CO_2 and NH_3 into acetonitrile had been described previously.[20] The total current yield of the products (1, 2, 4) was 5.8%.

Results and Discussion

No data on the electrochemical efficiency of hydrogen gas-diffusion anodes in aprotic media in the presence of CO_2 or butadiene can be found in the literature. Polarization characteristics of a hydrogen gas-diffusion anode in acetonitrile and dimethylformamide with 0.1 M Bu_4NBF_4 as the supporting electrolyte (Figs. 2—4) point to its fairly high electrocatalytic activity in a nonaqueous medium. The presence of CO_2 in the same electrolytes scarcely influences the ionization current of dihydrogen; it decreases substantially only in the presence of butadiene (see Fig. 4, curves 3 and 3'). Upon prolonged galvanostatic electrolysis (20—30 h, I = 6.3 mA cm^{-2}), the electrode potential increases from 395 to 780 mV (Fig. 5).

The preparative-scale electroreduction of CO_2 in the presence of butadiene in aprotic media in a diaphragmless cell with a hydrogen anode* gives only traces of formic acid (see above, entry 1). In a two-compartment cell, formic acid is produced as the main reaction product. In view of the kinetic data obtained, the absence of noticeable amounts of formic acid in a diaphragmless cell can be explained by high anodic potentials of the gas-diffusion electrodes due to the absorption of butadiene on the anode[21,22] and by the possible electrooxidation of formic acid at 0.8 V.[8]

Thus, the data obtained here confirm the feature noted in the vast majority of publications, namely, that electroreduction of CO_2 in the absence[11—17] or in the presence of an olefin acting as an acceptor[1,4,8—10,23] gives carboxylates only in the case where a metal or ammonium cation serves as the counterion. If H^+ is the counterion, similar reactions yield formic acid.

In our opinion, the role of the counterion is due to its influence on the reactivity of the key intermediate of the reaction, $CO_2^{\cdot -}$ radical anion. This influence can be interpreted as follows.

The $CO_2^{\cdot -}$ radical anion can be represented as two structures in which either the unpaired electron (A) or the negative charge (B) is localized on the carbon atom.

     A   A'   B   B'

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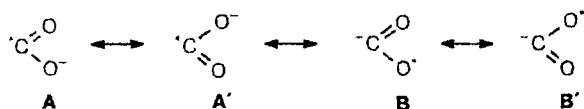
* A typical experiment with a hydrogen anode and the preparation and testing of the activity of a hydrogen anode is given in the Experimental section.

The reactions of both contributing structures, A and B, with metal or ammonium cations give rise to ion pairs in which the cations migrate reversibly between the O and C anionic centers; thus the $CO_2^{\cdot -}$ radical anion retains its ability to undergo subsequent chemi-
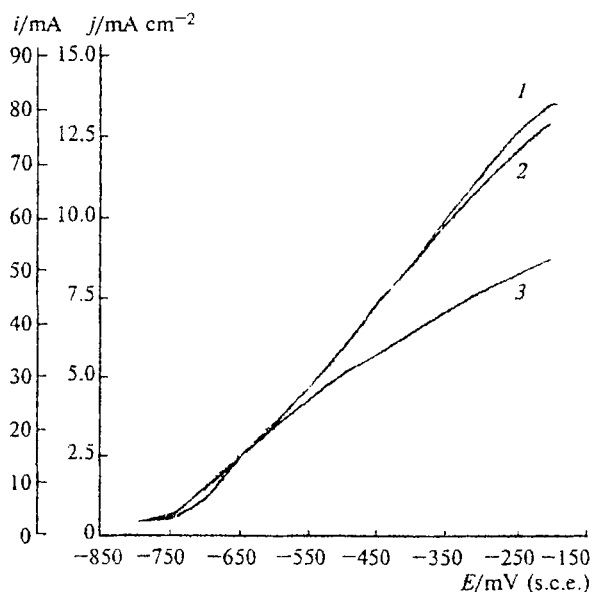
Fig. 2. Polarization curves of the hydrogen gas-diffusion electrode (S = 7 cm^2) in AN with 0.1 M Bu_4NBF_4 as the supporting electrolyte (1) and in the same solution saturated with CO_2 at 1 atm (2, 3). Curve 3 was recorded after preliminary anodic polarization for 14 h at E = −195 mV (pressure of H_2 120 mm H_2O, potential sweep rate 0.5 mV s^{-1}, type A electrode).
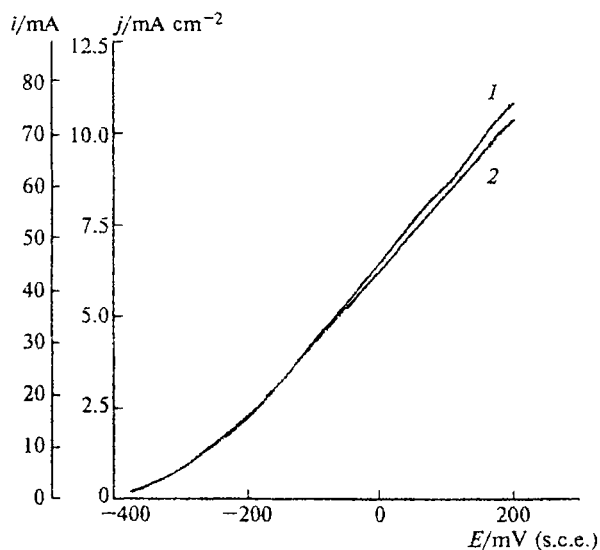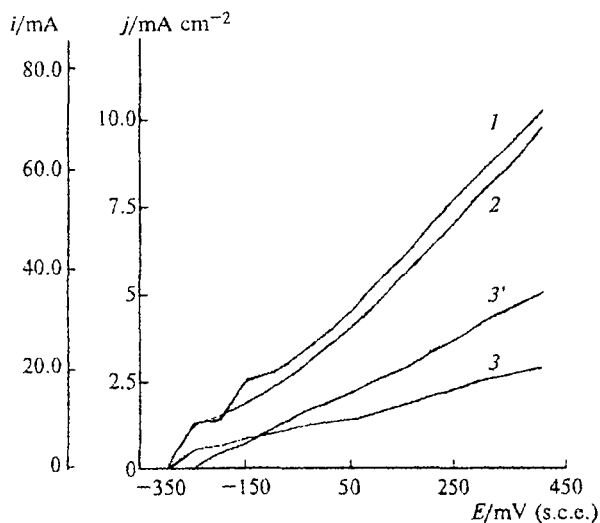
Fig. 3. Polarization curves of the hydrogen gas-diffusion electrode (S = 7 cm^2) in DMF with 0.1 M Bu_4NBF_4 as the supporting electrolyte (1) and in the same solution saturated with CO_2 at 1 atm (2) (pressure 120 mm H_2O, potential sweep rate 0.5 mV s^{-1}, type A electrode).

Fig. 4. Polarization curves of the hydrogen gas-diffusion electrode ($S = 7$ cm^2) in DMF with 0.1 M Bu$_4$NBF$_4$ as the supporting electrolyte (*1*), in the same solution saturated with CO_2 at 1 atm (*2*), and in the same solution saturated with CO_2 and 1,3-butadiene at 1 atm (*3, 3'*). Curve *3'* was recorded after preliminary galvanostatic electrolysis at a current density of 6.3 mA cm^{-2} ($I = 44$ mA) for 27 h (pressure of H_2 200 mm H_2O, potential sweep rate 0.5 mV s^{-1}, type *B* electrode).
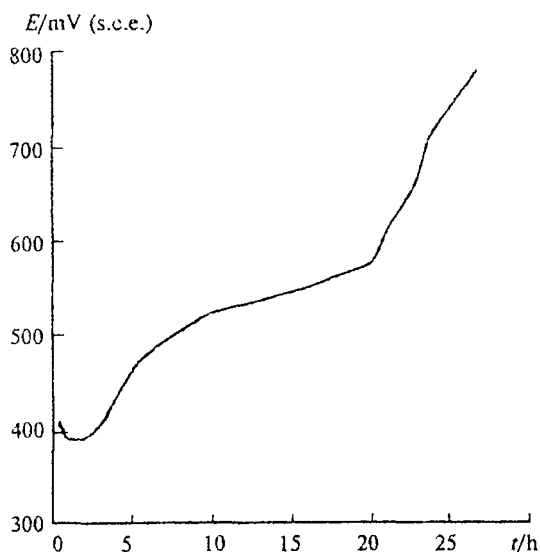
Fig. 5. Chronopotentiometric curve of a hydrogen gas-diffusion electrode during electrolysis at a constant current density, 6.3 mA cm^{-2} ($I = 44$ mA) in DMF with 0.1 M Bu$_4$NBF$_4$ saturated with CO_2 and 1,3-butadiene at 1 atm; type *B* electrode.

cal transformations as a C-centered radical (structure **A**). In the case of proton, its migration from the O atom (structure **A**) to the C atom (structure **B**) results in the formation of a strong covalent CH bond and thus yields a formyloxy radical. Under the conditions of a cathodic process, the only pathway for the subsequent

chemical transformation of this species is reduction to the formate anion.

The influence of the nature of the cation on the course of cathodic carboxylation of butadiene is illustrated by the electrolysis carried out using a hydrogen anode but in the presence of metal cations. The addition of MgO, CaO, or BaO to the electrolyte (in the presence of solvated protons, this leads to the generation of Mg^{2+}, Ca^{2+}, or Ba^{2+} ions upon the chemical reaction of the proton with the corresponding solid oxide, insoluble in water) resulted in the formation of products of butadiene carboxylation, 3-pentenoic and hexenedioic acids (see entry *2*).

The products of carboxylation of olefins (isoprene and butadiene) were also obtained in various procedures of electrolysis carried out with a hydrogen anode and with generation of a hydrated proton by adding triethylamine to the catholyte or ammonia to the anolyte (see entries *3* and *4*).

A specific type of hydrogen anode has been the oxidation of anhydrous NH$_3$ in an aprotic medium at a platinum anode in a diaphragmless cell. Electrooxidation of ammonia affords N$_2$ and protons, which form ammonium ions with excess ammonia; these ions act as counterions for the $CO_2{}^{\cdot-}$ radical anions. In this case, too, the products of carboxylation of butadiene, 3-pentenoic, hexenedienoic, and decadienedioic acids, were detected among the products (see entry *5*).

In all the electrocarboxylation procedures using a hydrogen anode, evolution of H$_2$ resulting from proton discharge occurs as a parallel cathodic process; in nonaqueous, initially aprotic media, this occurs at potentials ranging from -1.4 to -1.6 V vs s.c.e., *i.e.*, somewhat earlier than the electroreduction of carbon dioxide. The latter fact accounts for the very low yields (3.5—5.8%) of the butadiene carboxylation products.

Thus, the addition of reagents capable of interacting with protons to generate metal or ammonium ions to the electrolyte enables preparation of C-carboxylation products in the above-described reactions, and this confirms the conclusion, based on the published data, that the counterion plays a key role in the cathodic carboxylation of olefins.

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