

Electrosynthesis of Allene (Propadiene) and of Propyne (Methylacetylene) through the Anodic Decarboxylation Reaction (Part 2)

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The anodic decarboxylation reaction is a general reaction that can be applied with success to several suitable precursors. This work presents the electrochemical synthesis of allene by anodic oxidation of potassium itaconate. It is also shown that the anodic oxidation of potassium citraconate produces propyne. In both cases, unsaturated hydrocarbons were formed together with CO and CO₂. The electrooxidation of potassium crotonate leads to a simultaneous formation of propyne and allene (the latter in considerably smaller amounts than the former). Also in this case, formation of the unsaturated hydrocarbons is accompanied by the formation of CO and CO₂.

Key words: anodic decarboxylation, electrosynthesis, allene, propyne.

INTRODUCTION

According to the old literature,¹ the Kolbe coupling reaction does not occur in the anodic oxidation of unsaturated dicarboxylic acids such as maleic and fumaric^{2,3} or citraconic acids.^{4,5} The anodic oxidation of these substrates has received very limited attention and only a long time ago. It is interesting to note that none of the past or recent books and reviews on organic electrochemistry and the Kolbe reaction report the anodic oxidation of unsaturated dicarboxylic acids.^{6–12}

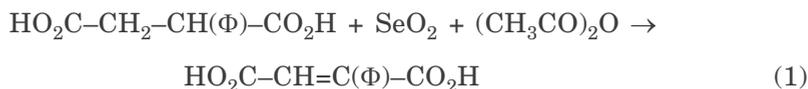
However, it is known that the anodic oxidation of unsaturated dicarboxylic acids causes a decarboxylation reaction and the formation of unsaturated

hydrocarbons like acetylene (from maleic and fumaric acids) or propyne (from citraconic or methylmaleic acid). No yields were reported in the old literature.¹⁻⁵

Recently, we have re-examined the anodic decarboxylation reactions of some selected unsaturated substrates.¹³⁻¹⁵ We have focused our attention on maleic, fumaric and acetylenedicarboxylic acids and have made a detailed qualitative and quantitative analysis of the anodic products formed by FT-IR spectroscopy of the anodic gases and other non-volatile products.^{13,14} These studies^{13,14} have confirmed the anodic formation of acetylene together with CO₂ when fumaric or maleic acids are anodically oxidized. We have also detected for the first time the formation of significant amounts of carbon monoxide CO, which has never been reported before. Typically, the composition of anodic gases produced from fumaric acid oxidation^{13,14} varies from 23% to 31% (volume fraction, φ) of acetylene and about 20% of carbon monoxide. The remaining amount was CO₂. On the other hand, maleic acid gives^{13,14} a lower acetylene yield ($\varphi = 10\%$ – 20%) and a very high amount of carbon dioxide (over 70%), the remaining amount to 100% being CO. No acetylene was produced from the anodic oxidation of acetylenedicarboxylic acid,¹⁴ but exclusively CO and CO₂ ($\varphi = 20\%$ and 80% , respectively). Surprisingly and contrary to the common knowledge, we have documented for the first time¹⁴ that in addition to the formation of the gaseous products mentioned above, the anodic oxidation of maleic, fumaric and acetylene dicarboxylic acids leads also to the formation of unsaturated coupling products having conjugated double and triple bonds. Evidence of this unexpected coupling reaction is given by the progressive darkening of the solution in the anodic compartment of the H-shaped cell, by the increasing optical density of the anolyte solution with the development of new absorption bands at 308 and 360 nm when acetylene-dicarboxylic acid is electrooxidized or new bands at 320 and 340 nm when maleic or fumaric acids are used, respectively. These new absorption bands grow as a function of the amount of current passed into the cell, showing that the formation of new products is dependent on the reactions occurring at the anode. In some cases, even a black-brown carbonaceous solid on the anode was recovered. The spectral analysis with infrared spectroscopy of both electrooxidized anodic solutions or the black solid carbon deposit showed definitively that the coupling product is a material containing acetylenic triple bonds and having a polyyne-polyene type of structure.¹⁴ Thus, we can state now that the Kolbe reaction applied to special substrates having unsaturated double bonds attached to the carboxylic groups, such as maleic, fumaric and acetylenedicarboxylic acids, leads to the formation of CO₂, CO, acetylene and acetylenic coupling products.

We have also shown for the first time that it is possible to prepare phenylacetylene by anodic oxidation of phenylmaleic acid.¹⁵ Phenylacetylene is a

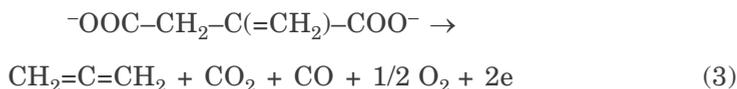
valuable monomer that is essential in the preparation of conducting polymers. A commonly used route to phenylacetylene involves cinnamic acid as the starting raw material and several steps are needed to reach phenylacetylene.¹⁶ Alternatively, phenylacetylene can be prepared by the styrene bromination-debromination route.¹⁶ Instead, we have shown that phenylacetylene can be prepared by anodic oxidation of phenylmaleic acid, although the yields are relatively low because the process has not been optimized. Hence, at this stage we cannot affirm that the electrosynthesis of phenylacetylene is superior to the classic routes both because of the low yields and also because phenylmaleic acid is not readily available. In fact, phenylmaleic acid is not commercially available, so we have prepared it from phenylsuccinic acid according to the following schematic reaction:¹⁷



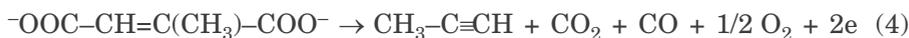
which involves the dehydrogenation of phenylsuccinic acid induced by selenium dioxide. By anodic oxidation of potassium phenylmaleate, phenylacetylene is formed:



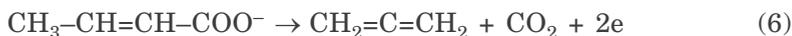
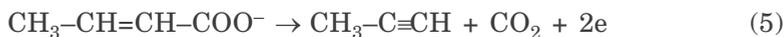
where (Φ) is a phenyl radical in all cases. Even if not reported in the above equation, carbon monoxide was also present as a secondary component. The above reaction is very general and many valuable molecules can be produced from a suitable precursor. For instance, in the present work we will show that allene can be produced from the anodic oxidation of potassium itaconate (schematically):



When citraconic acid (methylmaleic acid) is electrolytically oxidized, propyne (methylacetylene) is produced (schematically):



while by using crotonic acid as the starting substrate, allene and propyne are formed simultaneously (schematically):



but allene is present in small amounts.

EXPERIMENTAL

Itaconic acid, methylmaleic acid (citraconic acid) and crotonic acid were purchased from Aldrich/Fluka. FT-IR spectrometer used was a Perkin-Elmer 1710 while the UV-Vis spectrophotometer was a Shimadzu UV160A. A gas coulometer with the anodic compartment separated from the cathodic one by a fritted glass diaphragm was used in all experiments.¹⁸ The anodic gases were collected into a 10 cm path length IR cell and analyzed qualitatively and quantitatively by FT-IR spectrometry using published reference data.¹⁹⁻²¹ In fact, CO₂ was identified from its bands at 3730 and 3707 as well as 3628 and 3268 cm⁻¹ in conjunction with the doublet at 2362 and 2342 cm⁻¹.¹⁹⁻²¹ Quantitative estimations were made knowing that a 10 cm path length cell filled with CO₂ at 8 hPa gives an absorbance of $A = 0.131$ at 3730 cm⁻¹;¹⁹ CO, in turn, was identified from its bands at 2171 and 2121 cm⁻¹ and quantitatively estimated from the fact that at 8 hPa the absorbance is $A = 0.237$ units.¹⁹ The infrared absorbance of a characteristic band of a pure gas depends on its pressure inside a standard cell of a given path length. Knowing this absorbance at a known pressure, it is possible to estimate the partial pressure of a gas, in a mixture of gases from its actual absorbance. Knowing the partial pressure of a gas, it is possible to know its molar fraction. From Ref. 19 we have taken the absorbance of the characteristic bands at a known pressure of CO and CO₂ and applied these data to know the partial pressure of these two gases in our reaction mixtures. The correctness of this procedure was controlled by measuring the concentration of CO₂ also by its absorption on a Ba(OH)₂ solution to form Ba(CO₃) in a gravimetric procedure. A good agreement was found between the FT-IR estimation and the CO₂ amount found gravimetrically. Once the partial pressure and the concentration of CO and CO₂ were known, the concentration of the other gas propyne or allene was determined by difference. Allene was identified from its absorption band at 1973 cm⁻¹, which is due to the asymmetric C=C=C stretching.^{20,21} Conversely, propyne or methylacetylene were identified from their strong absorption bands at 3320 cm⁻¹ due to the ≡C-H stretching, the CH₃ stretching at about 2980 cm⁻¹ and from the bending of the C≡C-H at 630 cm⁻¹ and the bending overtone at 1250 cm⁻¹.^{20,21} The triple bond acetylenic stretching of propyne at 2130 cm⁻¹ is very weak in the infrared but very strong in the Raman spectra, so that it cannot be easily detected in the IR.^{20,21}

The anode material was in all cases made of a smooth platinum wire whose working surface was 0.4 cm². A constant DC tension was applied at the electrodes using the standard conditions considered typical of the application of the Kolbe reaction for preparative purposes.²² Despite the high tension applied, we have never worked under glow discharge electrolysis conditions.

Electrolysis of Potassium Itaconate

Itaconic acid (70.0 g) was dissolved in 200 ml of demineralized water. Then, 70.0 g of potassium hydroxide (85%, the remaining amount to 100% is water) was added to

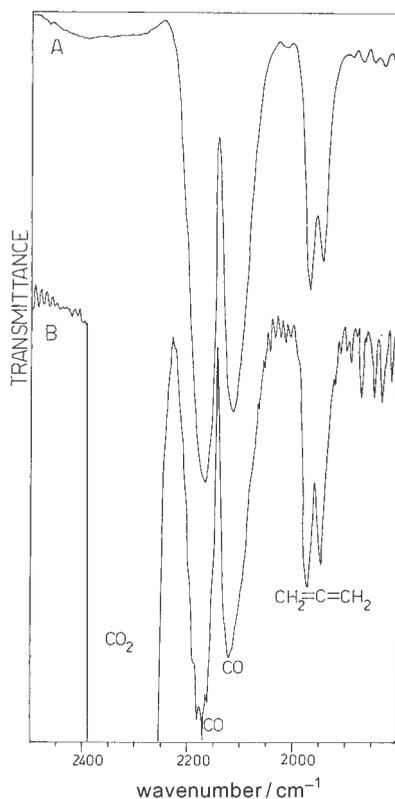


Figure 1. FT-IR spectra of the anodic gases generated from the electrooxidation of potassium itaconate. A represents the spectrum of the gases after the CO_2 absorption over $\text{Ba}(\text{OH})_2$ solution. B represents the spectrum of the crude gases evolved.

produce a solution of dipotassium itaconate. The solution was electrolyzed in the coulometer at 56 V and 1.3 A. Typically, the volume ratio between the cathodic gas (essentially hydrogen) and the anodic gases was 1.8 : 1; by prolonging the electrolysis, the ratio decreased to 1.5 : 1 or even lower. Working with 30 V and about 0.5 A, the volume ratio of the cathodic and anodic gases was approximately the same as that observed at 56 V. Even after prolonged electrolysis, the darkening of the anodic solution was negligible, showing that the formation of coupling products was really a minor reaction. This was not the case of other substrates where abundant coupling products were formed.¹⁴ The FT-IR spectrum of the anodic gas is shown in Figure 1; for discussion of components see the »Results and Discussion« section. Carbon dioxide was determined also gravimetrically by absorption in $\text{Ba}(\text{OH})_2$.¹⁴

Electrolysis of Potassium Citraconate (Methylmaleate)

Citraconic anhydride is not soluble in water but can be solubilized in an alkaline solution. KOH (79.5 g, 85% active) was dissolved in 200 ml of demineralized water

and then the anhydride was added to the solution and dissolved to form the dipotassium salt of citraconic acid. The electrolysis was conducted in the coulometer at 36 V and 0.44 A. As in the previous case, the volume ratio of the cathodic and anodic gases was determined and the analysis of the anodic gases was made by FT-IR spectroscopy and gravimetrically with $\text{Ba}(\text{OH})_2$.

Electrolysis of Potassium Crotonate

Crotonic acid (40.0 g) was added to a solution of 30.0 g of KOH (85% active) in 200 ml of demineralized water. After the dissolution of crotonic acid, the solution was electrolyzed in the coulometer at 36 V and 0.3 A. The gases evolved were collected and analyzed as described above. Darkening due to the formation of coupling products was not observed in the anode compartment in this case, even after prolonged electrolysis. Instead, the solution in the cathode compartment darkened very easily becoming orange-brown. The UV-Vis spectrum of the darkened cathodic solution shows three maxima at 345, 350 and 395 nm, which can be explained by the reduction of crotonic acid to crotonaldehyde followed by the alkali-catalyzed condensation reaction of this molecule with crotonic acid leading to 2,4,6-octatrienoic acid.

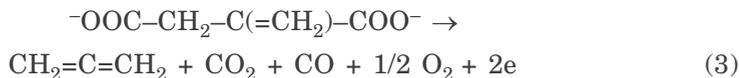
RESULTS AND DISCUSSION

About the Products Formed from the Anodic Oxidation of Potassium Itaconate

The chemical structure of itaconic acid resembles that of methylmaleic acid but it is characterized by an external double bond: the $=\text{CH}_2$ moiety. The FT-IR spectrum of the anodic gases evolved from itaconic acid (Figure 1) show that the three main products of the anodic oxidation are CO_2 , CO and allene $\text{CH}_2=\text{C}=\text{CH}_2$. No acetylenes were formed and detected. All gases were qualitatively detected by their characteristic bands in the infrared spectrum and quantitatively estimated from their absorption in the infrared spectrum (see experimental section for the procedure used).

Additionally, the CO_2 amount was also determined gravimetrically by passing a known volume of the anodic gas into a solution of $\text{Ba}(\text{OH})_2$ and weighing the amount of $\text{Ba}(\text{CO}_3)$ precipitated from it. A reasonable agreement was found between the determination of CO_2 by infrared spectroscopy and by gravimetry. Figure 1 illustrates the procedure used to conduct the quantitative analysis of CO_2 . When the anodic gases were washed into a solution of $\text{Ba}(\text{OH})_2$, all the CO_2 originally contained in the gases (see Figure 1B) was fixed as carbonate and the emerging gases (see Figure 1A) were completely free from CO_2 . The formation of allene, CO_2 and CO can be described schematically from the Eq. (3) and formally involves the oxidation of the carboxylic groups to CO and oxygen and to CO_2 while the formal oxidation state of the other three carbon atoms of the itaconic acid molecule does

not change at all before and after the oxidation, remaining -2 for two carbon atoms and zero for the otherone, like in the final product allene:



Most probably, as discussed elsewhere,¹⁴ the formation of CO takes place as a secondary reaction involving the oxidation of part of the allene as soon as it is formed at the anode. Therefore, the real anodic reaction leading to the products detected could be:



and



Notwithstanding that Eqs. (7) and (8) are more probable than Eq. (3), the distribution of gases detected is very close to that theoretically expected from Eq. (3). In fact, the results (ρ) are: $\text{CH}_2=\text{C}=\text{CH}_2$ 28.6% (experimental), 28.6% (theoretical); CO_2 33.5% (exp.), 28.6% (theor.); CO 26.1% (exp.), 28.6% (theor.); O_2 11.8% (exp.), 14.3% (theor.).

Assuming that Eq. (3) has really taken place at the anode, assuming that the unique reaction at the cathode was the evolution of hydrogen, from the volume ratio measured at the coulometer between the cathodic and the anodic gases, it is possible to estimate the current yield of the anodic gases. Since the volume ratio cathodic/anodic gases was found experimentally to be about 1.8 : 1 and since 2 electrons were involved in both cathodic and anodic reactions, the current yield of anodic gases over the cathodic was between 52.6% to 58.8%.

*About the Products Formed from the Anodic Oxidation
of Potassium Citraconate (Methylmaleate)*

Citraconic acid has a chemical structure that is analogous to that of maleic acid but one hydrogen atom at the double bond is substituted by a methyl group. We have already shown that maleic acid produces acetylene and other products by anodic oxidation^{13,14} while the electrolysis of the phenyl-substituted phenylmaleic acid produces phenylacetylene.¹⁵ Thus, it is obvious to expect the production of propyne or methylacetylene from the anodic oxidation of citraconic acid. Figure 2 shows the FT-IR spectrum of the anodic gases produced by the electrooxydation of citraconic acid in alkaline

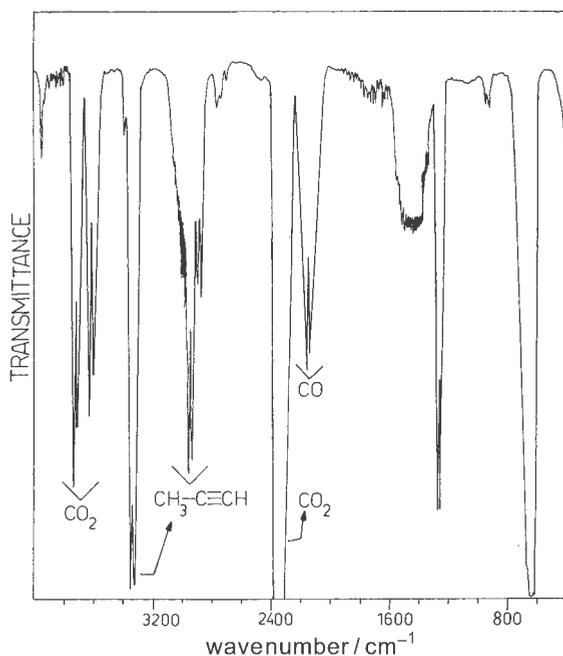
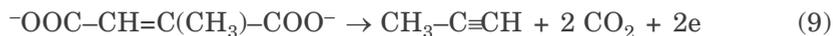


Figure 2. FT-IR spectrum of the anodic gas evolved from the electrooxidation of potassium citraconate.

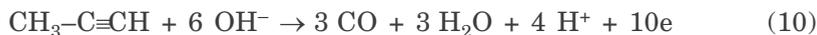
solution. Propyne can be easily detected from the two characteristic absorption bands at 3320 cm^{-1} due to the acetylenic $\equiv\text{C}-\text{H}$ stretching and other bands, as already stated in the experimental section. Copious amount of CO_2 can be easily detected from the strong band at 2363 and by the bands between 3750 and 3600 cm^{-1} .^{19,22} The sources of CO_2 are the carboxyl groups of the dicarboxylic anion. Carbon monoxide is also formed, as detected by its typical IR bands^{19,22} at 2171 and 2121 cm^{-1} in the spectrum of Figure 2. The formation of CO was also detected in previous investigations involving the anodic oxidation of potassium maleate and fumarate^{13,14} and, as discussed both in the case of itaconic acid and elsewhere,¹⁴ it can be attributed to secondary anodic oxidation reactions of the organic substrates. Thus, the reaction scheme Eq. (4)



does not necessarily reflect the real reaction step, which may be alternatively described by the following reactions:¹⁴



and



where Eq. (10) represents the anodic oxidation to carbon monoxide of part of the propyne formed.

It is fascinating to note that, like in the case of itaconic acid, the formal oxidation state of the three carbon atoms inside the citraconic acid molecule (hence with the exclusion of the two carbon atoms bearing the carboxylic groups) does not change before and after the electrooxidation. Thus, the formal oxidation state of the carbon atoms bearing the carboxylic groups pass from +3 to +4 in Eq. (9) while the formal oxidation state of the other three carbon atoms originally at -1, 0 and -3, respectively, remains unchanged also in the final product propyne.

Assuming again that Eq. (4) is the reaction that takes place at the anode, we can compare the composition of the anodic gases theoretically expected and those observed experimentally. The agreement is not so good as in the case of itaconic acid, but also here the volume of the hydrocarbon produced is close to the theoretical. The results are: propyne 29.4% (exp.), 28.6% (theor.); CO₂ 39.3% (exp.), 28.6% (theor.); CO 20.7% (exp.), 28.6% (theor.); O₂ 10.6% (exp.), 14.3% (theor.).

Assuming also here that the unique reaction at the cathode is the formation of hydrogen, at anode Eq. (4), we can make an estimation of the current yield. In the case of citraconic acid, the volume ratio between cathodic and anodic gases was 7.2 : 1 and after prolonged electrolysis it approached 4 : 1. Therefore, the estimated current yield for the production of anodic gases is low: only 13.9%, which could grow up to 25%. Probably, other secondary reactions take place at the anode, for example, coupling reactions like in the cases reported in a previous work¹⁴ or, simply Eq. (4) is not the best model to describe the anodic reactions taking place at the anode when citraconic acid is the substrate.

About the Products Formed from the Anodic Oxidation of Potassium Crotonate

Crotonic acid is an α,β -unsaturated monocarboxylic acid. Figure 3 shows the products formed from its anodic oxidation. In addition to the usual products observed in all our studies of CO and CO₂, propyne is the main hydrocarbon product and allene is formed too but in smaller amounts.

The experimental results of our analysis are the following (vol. fractions): propyne 20.3%, allene 2.6%, CO₂ 58.1%, CO 13.6%, O₂ 5.4%.

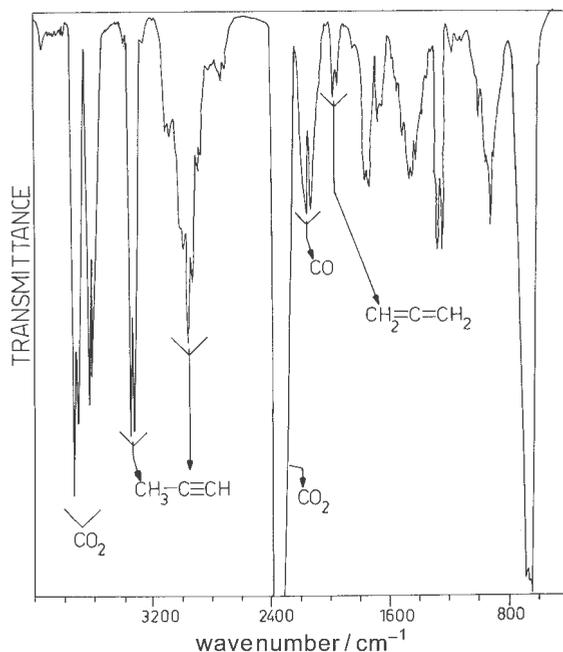
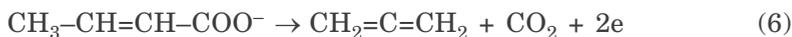
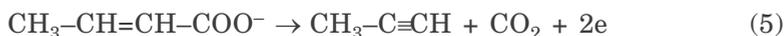
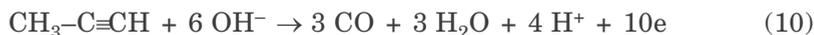


Figure 3. FT-IR spectrum of the anodic gases evolved from the electrooxidation of potassium crotonate.

Thus the reactions taking place at the anode are:



and the formation of CO could be ensured by these two reactions:



In the case of crotonic acid, the formation of propyne and allene involves also a change in the formal oxidation state of the three carbon atoms not bearing carboxylic groups. In fact in crotonic acid, the formal oxidation state $\text{CH}_3\text{-CH=CH-COOH}$ is -3 , -1 , -1 and $+3$ (carboxylic group), respectively; the propyne formation involves the oxidation of the central atom from -1 to 0 : in fact, for $\text{CH}_3\text{-C}\equiv\text{CH}$ we have formally -3 , 0 and -1 . The situation is

more complicated in the case of allene $\text{CH}_2=\text{C}=\text{CH}_2$ where we have a formal oxidation state of -2 , 0 and -2 . This means that the non-carboxylated part of the crotonic acid molecule should undergo simultaneously two oxidations and one reduction. Thus, the oxidation that leads to allene formation appears to be a more complicated process than the oxidation leading to the formation of propyne (starting from crotonic acid) and this may be the reason why allene is formed only in a minor quantity from crotonic acid and why propyne is the main hydrocarbon product.

Also in the case of crotonic acid electrolysis, the cathodic gas volume largely exceeds that of the anodic gases. Experimentally, the cathodic/anodic volume ratio was found to be $2.2 : 1$ to $2.4 : 1$.

CONCLUSIONS

We have shown how versatile is the anodic decarboxylation reaction, which can be applied to some uncommon substrates to produce somewhat exotic molecules such as allene and propyne. The present work represents a modern investigation and application of an old discovery. After having reviewed our early results on the application of the electrooxidation of unsaturated dicarboxylic acids under the Kolbe conditions to maleic, fumaric and acetylenedicarboxylic acids and after having discussed the new discoveries we have made in this field, namely the quantitative determination of the acetylene formed, the presence of CO together with the well known CO_2 and the fact that coupling products like polyynes are formed from the anodic oxidation of these substrates, we have presented a further application of a concept – the anodic decarboxylation reaction. We have demonstrated that this reaction is very general and can be applied to numerous and somewhat rare substrates.

By anodic decarboxylation reaction acetylene can be obtained from potassium maleate and fumarate,¹⁴ phenylacetylene from potassium phenylmaleate¹⁵ and, as shown in the present work, allene from potassium itaconate and propyne from both potassium citraconate and from potassium crotonate. The yields seem quite good and, although not optimized, suggest that the anodic decarboxylation reaction could find application as a synthetic tool.

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SAŽETAK

Elektrosinteza alena (propadiena) i propina (metilacetilena) reakcijom anodne dekarboksilacije (II. dio)

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Reakcija anodne dekarboksilacije uspješno se može primijeniti na mnoge pogodne prekursore. Opisana je elektrokemijska sinteza alena anodnom dekarboksilacijom kalijeva citrakonata. Također se pokazalo da se pri anodnoj oksidaciji kalijeva citrakonata stvara propin. U oba slučaja nezasićeni ugljikovodici nastali su zajedno s CO i CO₂. Elektrooksidacija kalijeva kronata vodi do istovremenog stvaranja propina i, u znatno manjoj količini, alena. I u tom je slučaju nastanak nezasićenih ugljikovodika popraćen stvaranjem CO i CO₂.