# A New Approach to the Anodic Decarboxylation of Unsaturated Dicarboxylic Acids. Part 1: Fumaric, Maleic and Acetylenedicarboxylic Acids.

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The dipotassium salts of maleic, fumaric and acetylenedicarboxylic acids were electrooxidized and the reaction products were analyzed qualitatively and quantitatively by UV/VIS and FT-IR spectroscopy. Acetylene, carbon dioxide and carbon monoxide, along with polyynes, are the products obtained from maleic and fumaric acids. The best acetylene yields are obtained from fumaric acid and not from maleic acid, which gives the highest yield of carbon dioxide. High concentration and high current density lead to the formation of carbonaceous matter containing carbyne recognizable by triple-bond stretching. Anodic oxidation of acetylenedicarboxylic acid produces only a mixture of carbon dioxide, carbon monoxide and soluble polyynes; no free acetylene was detected.
A total of 15 chemical reactions with their free energy were studied to explain the reaction products of anodic oxidation.

*Key words:* unsaturated dicarboxylic acid, anodic oxidation, anodic gases analysis, carbyne, FT-IR spectroscopy, UV/VIS

## INTRODUCTION

The well-known and widely studied Kolbe reaction is an electrolytic decarboxylation followed by dimerization of alkyl radicals and involves several steps.[1–5]

$$R\text{–}COO^- \rightarrow R\text{–}COO^* + e^-$$
$$R\text{–}COO^* \rightarrow R^* + CO_2$$
$$2\ R^* \rightarrow R_2$$
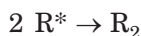
which can be represented schematically by the general reaction:

$$2 \ RCOO^- \rightarrow R–R + 2 \ CO_2 + 2e^-$$
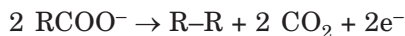
although other reactions, like further oxidation of alkyl radicals to carbonium ions can take place:

$$R^* \rightarrow R^+ + e^-$$

Platinum anode remains essential to affording R radicals (and not $R^+$).

It has been shown that the Kolbe reaction does not occur or gives poor yields of dimer if the R group bears an α substituent capable of stabilizing the carbonium ion formed during the anodic oxidation or if R is an aryl or an α,β-unsaturated acid.[1,2,4,5]

Another case where the Kolbe coupling reaction seems not to occur is the anodic oxidation of unsaturated dicarboxylic acids such as maleic,[6,7] fumaric[6,7] and citraconic acids.[8,9] The anodic oxidation of these substrates has received very limited attention and only long ago; the predominant reaction in Kolbe conditions was a decarboxylation reaction with formation of acetylene (from maleic and fumaric acids) or propyne (from citraconic or methylmaleic acid) in not well defined yields. Acetylenic compounds are also formed in cathodic elimination reactions.[10] Moreover, recent reviews on electrosynthesis normally neglect reporting the behaviour of unsaturated dicarboxylic acids under anodic oxidation conditions,[3–5,10,11] probably due to lack of recent and convincing data.

In this and in the following papers, we have re-examined the anodic decarboxylation reactions of unsaturated dicarboxylic acids and have made a detailed qualitative and quantitative analysis of the products formed by FT-IR and UV/VIS spectroscopy in anodic solutions and by FT-IR spectroscopy and classical gas analysis in anodic gases. Current yields have been estimated.

## EXPERIMENTAL

Maleic and fumaric acids were obtained from C. Erba reagenti, acetylenedicarboxylic acid was from Aldrich. FT-IR spectra were obtained on a Perkin-Elmer 1710 spectrometer, UV/VIS spectra on a Shimadzu 160A spectrophotometer.

### UV/VIS Spectra of Anodic Solutions

In this part of the work, electrolysis was carried out in an H-shaped cell with the anode separated from cathode by fritted glass. The anodic solution flowed continuously into a quartz cuvette placed into the spectrophotometer by means of a peristal-

tic pump. The anode was a smooth Pt wire having an apparent area of 0.62 cm$^2$. After a well defined quantity of electricity was passed, the electrolysis was stopped, the anodic solution was stirred and then the UV/VIS spectrum was recorded. These operations were repeated several times and absorption curves like those shown in Figure 1 were obtained. A cuvette with the non electrolyzed solution was placed in the reference beam of the spectrophotometer for all experiments.

In all experiments, the temperature was kept at 30 °C, the voltage was 30 V and the concentration of dipotassium salt of fumaric acid or maleic acid was 3.0 M whereas the concentration was 0.62 M for the dipotassium salt of acetylenedicarboxylic acid. In all cases, the anodic volume was 50 mL. Current densities used in these experiments were as follows: fumaric acid 7.4 A/cm$^2$, maleic acid 1.1 A/cm$^2$ (first run) and 6.3 A/cm$^2$ (second run), acetylenedicarboxylic acid 4.0 A/cm$^2$.

## FT-IR Spectra of Anodic Solutions and of the Dark Insoluble Matter Collected on the Anode

*Fumaric acid:* Using the same apparatus as described above, upon prolonged electrolysis of the 3.0 M solution, working at 2.7 A/cm$^2$, deposition of a solid (presumably carbonaceous matter) on the anode occured. This material was collected (about 20 mg) and studied by FT-IR spectroscopy (see results and discussion and Figure 6). The anodic solution became brown and then dark-brown. FT-IR spectra (from 4000 to 1100 cm$^{-1}$) were recorded in the dark-brown anodic solution by using CaF$_2$ windows and the spectrum of the non electrolyzed solution was subtracted from that of the anodic solution. Two new bands were observed: the first one strong at 3175 cm$^{-1}$ and the other one medium-weak at about 2100 cm$^{-1}$.

*Maleic acid:* Upon prolonged electrolysis in the same H shaped cell as described above, of the 3.0 M solution at 3.2 A/cm$^2$, the anodic solution became dark-brown as in the case of fumaric acid but there was no deposition of black material on the anode. The FT-IR spectrum of the crude anodic solution (using CaF$_2$ windows) showed no evidence of any new bands. The anodic solution was then partially acidified with 10% HCl and the black precipitate which formed first was collected by filtration (yield 0.7 g). The FT-IR spectrum of this product is shown in Figure 6.

*Acetylenedicarboxylic acid*: Prolonged electrolysis (in the H-shaped cell) of the 0.6 M solution at 0.8 A/cm$^2$ caused the anodic solution to became yellow and then orange. Deposits were not observed on the anode nor were precipitates collected by partial acidification of the anolyte. A trend to electrocrystallization was observed at the anode especially at the beginning of the electrolysis. The crystals recovered were orange whereas acetylenedicarboxylic acid is white. However, FT-IR spectra of these crystals show that they are only acetylenedicarboxylic acid and the orange colour should be attributed to an impurity formed at the anode but present in a very low concentration.

## FT-IR Spectra of Anodic Gases and Gas Analysis

The electrolyses have been carried out in a Hofmann gas coulometer[12] having the anode compartment separated from the cathode compartment by fritted glass. Dipotassium fumarate, maleate, and acetylenedicarboxylic acid aqueous solutions have been electrolyzed on a smooth Pt wire anode.

Known volumes of the anodic gases collected in the gas buret of the gas coulometer were transferred into a 10 cm long IR gas cell and analyzed qualitatively and quantitatively in an FT-IR spectrometer (Perkin-Elmer 1710). Acetylene was identified from its bands at 3311 and 3268 cm$^{-1}$, carbon dioxide was identified from its bands at 3729, 3707, 3628 and 3598 and by the intense doublet at 2362 and 2342 cm$^{-1}$. [13,14] Carbon monoxide was identified from its bands at 2171 and 2121 cm$^{-1}$.[14] Absorption coefficients were deduced from Ref. 14.

Since carbon dioxide was the main component of all anodic gases, it was determined by absorption in a U-tube charged with soda-lime (from Fluka). The amount of carbon dioxide was deduced from the weight increase. The remaining anodic gases were determined directly by their absorbance in the normalized FT-IR spectrum. All results are reported in Table I.

## RESULTS AND DISCUSSION

### *Spectra of Anodic Solutions*

In this study, we have employed high concentrations of the dipotassium salts of maleic and fumaric acids, along with high current density. Our investigation involved also the dipotassium salt of acetylenedicarboxylic acid. In all cases, a progressive darkening of the anodic solution was observed during the electrolysis; therefore, formation of new chemical species in solution occurred in addition to the evolved gases, which will be discussed later.

Figure 1 shows that the UV/VIS spectra of the anodic oxidation products coming from acetylenedicarboxylic acid (Figure 1A), fumaric acid (Figure 1B), and maleic acid (Figure 1C) are not exactly the same. In fact, in the case of acetylenedicarboxylic acid, the initial maximum appears at 303 nm and is shifted later to 308 nm and an additional shoulder appears at 360 nm. Fumaric acid is characterized by a single and relatively narrow peak at 340 nm (Figure 1B) whereas maleic acid initially shows a peak at 310 nm with a pronounced shoulder at about 340 nm but in the following curves a relatively broad maximum appears at 319 nm. These spectra show that not exactly the same products are formed; however, they should be very similar in their chemical nature and should necessarily derive from coupling reactions between the precursor molecular fragments. Thus, they should have a polyene or polyynic nature. A more quantitative picture of the formation of these products is given in Figure 2 and Figure 3, where the absorbance data taken from Figure 1 have been plotted to show the direct relationship between the current passed in the cell and the formation of these coupling products. Figure 3 is of particular interest because it shows that the rate of formation of coupling products seems to be higher in the case of maleic acid than of fumaric acid; this means that the two isomers (respectively *cis* and *trans*) react in a different way and with different kinetics.
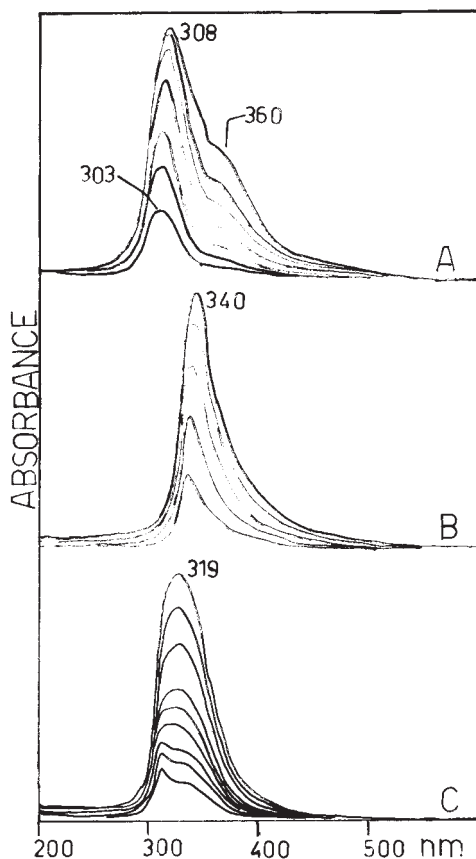
Figure 1. UV/VIS spectra of anodic solutions as a function of the degree of anodic oxidation. (A) Acetylenedicarboxylic acid K–salt, (B) K–fumarate, (C) K–maleate.

As reported in the experimental section, the FT-IR spectra of crude anodically oxidized solutions of fumaric acid showed two new bands at 3175 and 2100 $cm^{-1}$. These two new bands can be assigned to acetylenic compounds formed during the electrooxidation, the first being due to $\equiv$C–H stretching and the second to triple bond stretching.[13,14]

## Spectra of Anodic Gases and their Composition

Figure 4 shows the FT-IR spectra of anodic gases collected during the electrolysis of acetylenedicarboxylic acid (Figure 4A) and maleic acid (Figure 4B). Anodic gases produced from fumaric acid give similar spectra to those shown in Figure 4B. In these spectra, $CO_2$ can be easily identified by the intense band at 2363 $cm^{-1}$,[13,14] whereas carbon monoxide CO is easily
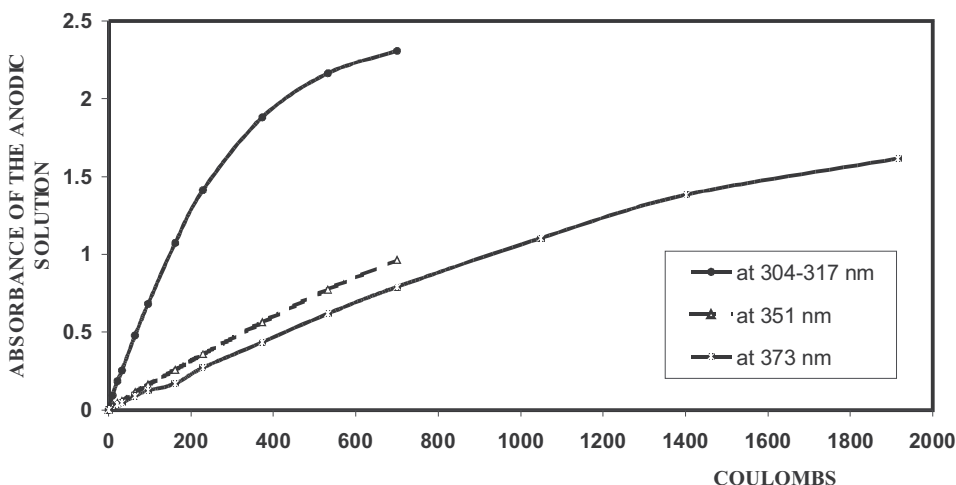
Figure 2. Graph obtained from absorbance data of Figure 1A recorded in acetylene-dicarboxilic acid (K-salt) solution, anodically oxidized.
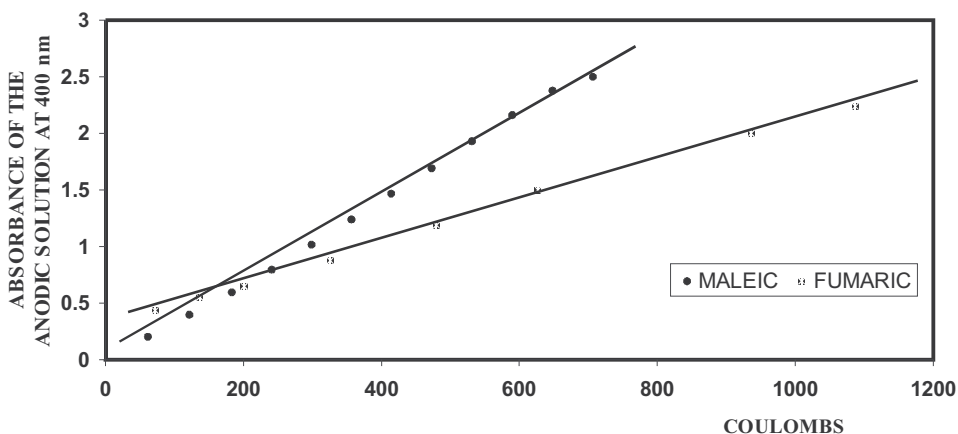


Figure 3. Graph obtained from absorbance data of Figures 1B and 1C recorded re-spectively in K–fumarate and K–maleate solutions, anodically oxidized.

detected by the characteristic doublet at 2171 and 2121 cm$^{-1}$. Thus, for the first time we are documenting that carbon monoxide is formed together with carbon dioxide during the electrolysis of maleic and fumaric acids; this fact has never been reported previously.[6,7] CO is also formed along with $CO_2$ during the electrolysis of acetylenedicarboxylic acid, but in this case no trace of acetylene was detected (Figure 4A), whereas acetylene is formed

abundantly during the electrolysis of maleic and fumaric acids, confirming early reports.[6,7] Acetylene is easily detected by its characteristic doublet at 3311 and 3268 cm$^{-1}$ (Figure 4B) due to $\equiv$C–H stretching.[13–14]

Concerning the quantitative analysis of anodic gases, as shown in Figure 5A, the $CO_2$ was completely eliminated by passing the anodic gases into a U-tube filled with soda-lime and measured by the weight increase of the
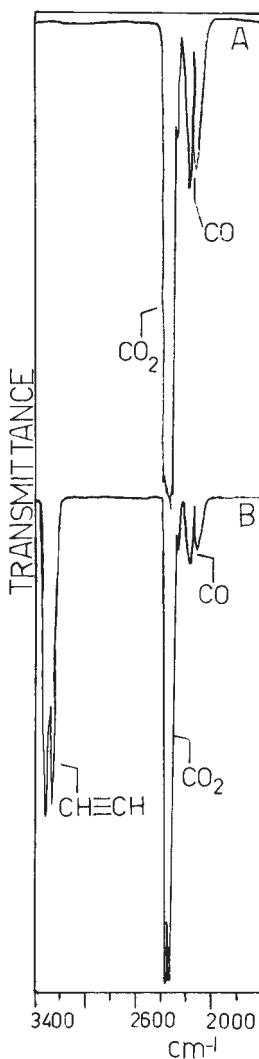


Figure 4. Qualitative FT-IR spectra of anodic gases. (A) Acetylenedicarboxylic acid (K-salt) produces a mixture of carbon dioxide and monoxide. (B) K–maleate produces a significant amount of acetylene.

soda-lime tube. The remaining gases emerging from the U-tube were collected in the FT-IR cell, and Figure 5A documents that all $CO_2$ was completely retained by the soda lime treatment. The FT-IR spectra of Figure 5A and 5B allowed us to measure the ratio between acetylene and CO from the known absorption coefficients.[14] From the total amount of $CO_2$ and the ratio of acetylene to CO, the composition per volume of anodic gases was then calculated and is reported in Table I. The results show that acetylenedicarboxylic acid and maleic acid give a huge quantity of $CO_2$, over 70% per volume,
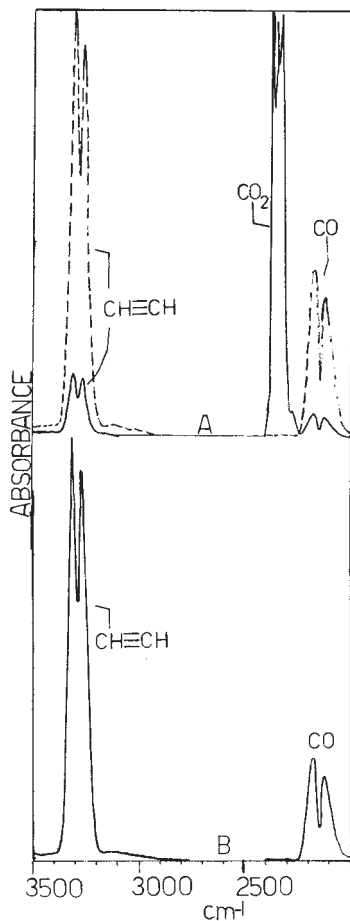


Figure 5. Quantitative FT-IR spectra of anodic gases (normalized spectra having scale-end = 1.5 absorbance units). (A full line) Spectrum on crude anodic gases from K–fumarate oxidation; (A dotted line) Spectrum of anodic gases from K–fumarate after $CO_2$ removal by soda-lime (see text). (B) FT-IR spectrum of anodic gases from K–maleate after $CO_2$ removal with soda-lime.

whereas fumaric acid gives lower amounts of $CO_2$, which increases when the solution is somewhat exhausted. The CO level is stable at about 20% per volume in the case of fumaric acid, and fumaric acid is also the precursor which gives the best acetylene yields per volume and per current in comparison to maleic acid which, in turn, gives the best current yields of $CO_2$. A curious relationship was found for the ratio of acetylene to CO yield as the function of current density. Unexpectedly, at least for maleic acid, low current density increases the yields of CO, whereas high current density increases the acetylene yield (see Table I).

Apparently, the best conditions for producing acetylene (Table I) involve the use of fumaric acid at a high concentration, and high current density should be employed–possibly over 4 A/cm$^2$; the use of a temperature around 40 °C is suggested. Under these conditions, the acetylene yield reaches 30% per volume.

Table I shows also that the ratio of cathodic to anodic gases is always larger than unity.

### About the Nature of the Anodic Coupling Products

In the previous section we confirmed that acetylene is formed from anodic oxidation of fumaric and maleic acids whereas no acetylene is found in the case of acetylenedicarboxylic acid. Thus, the coloured products we have detected during the anodic oxidation may have acetylenic nature and, being coupled products, they should have a polyynic nature. The FT-IR spectrum of a crude anodically oxidized solution of fumaric acid shows two acetylenic bands, as reported before. In Figure 6, we present further experimental evidence to confirm that, during maleic and fumaric acid electrooxidation, the anodic coupling reaction leads to polyyne chains. In fact, the black insoluble matter recovered at the anode after fumaric acid electrolysis shows two bands at 2190 and 1875 cm$^{-1}$ that are not present in the spectrum of fumaric acid itself (compare Figure 6B with 6A). These bands can be assigned respectively, to triple-bond stretching and to an allenic moiety.[13,14] Therefore, the spectrum suggests that the carbonaceous material that is formed contains both acetylenic and allenic carbyne. Carbyne is another carbon allotrope in addition to graphite, diamond and fullerenes[15] and up to now it has been prepared by several different techniques[16–20] but never in the way we are reporting here for the first time.

Figure 6B shows also that the spectrum of the carbonaceous product from fumaric acid is different from that of the original acid and shows the absence of the carboxylic band that appears at 1680 cm$^{-1}$ in the precursor (Fig-

TABLE I

Anodic gases composition, conditions, yields

| Dipotassium salt of: | Fumaric acid freshly prepared | Fumaric acid after some run | Maleic acid freshly prepared | Maleic acid freshly prepared | Maleic acid freshly prepared | Maleic acid prepared | Acetylene-dicar. acid |
|---|---|---|---|---|---|---|---|
| Initial conc. (M) | 2.3 | 2.3 | 2.3 | 3.0 | 2.3 | 2.3 | 0.57 |
| Tension (V) | 56 | 56 | 56 | 30 | 26 | 14.5 | 30 |
| Current density (A/cm$^2$) | 5 | 6 | 5 | 3.5 | 2.8 | 1.2 | 1 |
| Temperature (°C) | 42 | 40 | 32 | 32 | 25 | 25 | 25 |
| Volume ratio cathodic / anodic gases | 1.4 | 1.2 | 1.45 | 1.5 | 1.5 | 1.3 | 2.5 |
| Current yield on acetylene | 21.8 | 23.7 | 14.6 | | 7.9 | 7.3 | |
| Current yield on carbon dioxide | 17.0 | 20.3 | 24.7 | | 25.2 | 28.6 | |
| Anodic gas composition (% per volume): | | | | | | | |
| Carbon dioxide | 51.6 | 57.5 | 70.7 | 71.5 | 74.1 | 71.2 | 78.8 |
| Acetylene | 31.3 | 23.2 | 21.3 | 14.7 | 11.3 | 7.9 | 0 |
| Carbon monoxide | 17.1 | 19.2 | 8.0 | 13.8 | 14.6 | 20.9 | 21.2 |
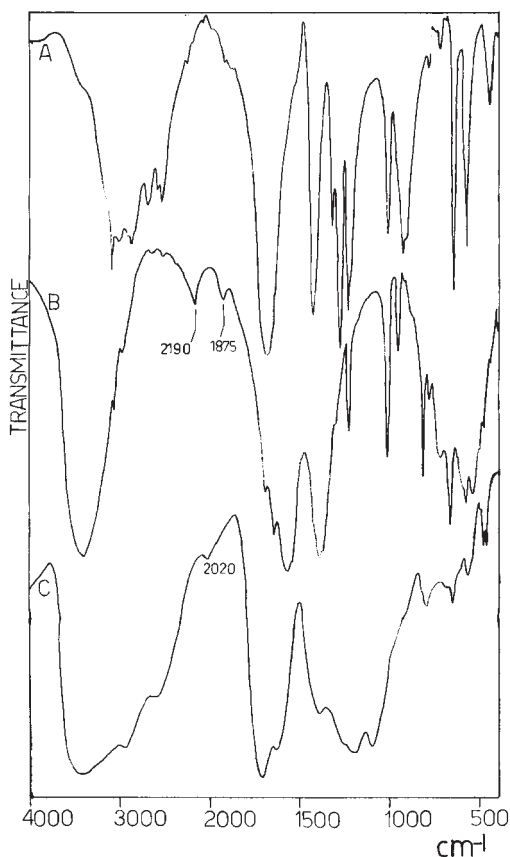
Figure 6. FT-IR Spectra of products of anodic oxidation of K–fumarate (B) and K–maleate (C) in comparison with the spectrum of pristine fumaric acid (A).
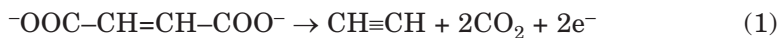
ure 6A) whereas now the maximum is shifted to 1570 cm$^{-1}$, suggesting the presence of double-bond stretching.

The coupling product from maleic acid is different from that of fumaric acid (Figure 6C *versus* 6B) but the general shape of the spectrum resembles that of a carbyne[14,15] and the weak band at 2020 cm$^{-1}$ also suggests the presence of allenic double bonds.

### *Discussion of the Anodic Reactions Involved*

To better explain what happens during the anodic oxidations studied in this paper, we have performed some thermodynamic calculations. The free energies of formation, $\Delta_f G^0$, of maleic and fumaric acids were estimated from

their heats of combustion taken from Ref. 21, which was used for the calcula-
tion of the enthalpy of formation, $\Delta_f H^0$, whereas the entropy, $\Delta_f S^0$, was cal-
culated according to Van Krevelen, by groups increments.[22] The two results
were combined to give the $\Delta_f G^0$. The estimated values were: $\Delta_f G^0$ = 164.11
Kcal/mol for maleic acid, whereas it is 168.51 Kcal/mol for fumaric acid. The
$\Delta_f G^0$ of acetylenedicarboxylic acid was estimated by means of the Van Kre-
velen method[22] and found to be –119.6 Kcal/mol. Using tabulated $\Delta_f G^0$ values
of all other chemical species[21] involved in the following reactions as well as
the value we already calculated[23] for acetylenic carbyne ($\Delta_f G^0$ = +45.12), we
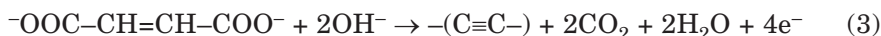get the following results:

$$^-OOC{-}CH{=}CH{-}COO^- \rightarrow CH{\equiv}CH + 2CO_2 + 2e^- \tag{1}$$

$$\Delta_r G^0 \text{ (maleic)} = +25.6 \text{ Kcal/mol}$$
$$\Delta_r G^0 \text{ (fumaric)} = +30.0 \text{ Kcal/mol}$$

$$^-OOC{-}CH{=}CH{-}COO^- \rightarrow CH{\equiv}CH + 2CO + O_2 + 2e^- \tag{2}$$

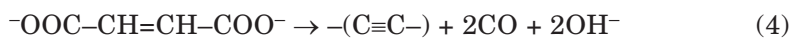$$\Delta_r G^0 \text{ (maleic)} = +148.5 \text{ Kcal/mol}$$
$$\Delta_r G^0 \text{ (fumaric)} = +152.9 \text{ Kcal/mol}$$

$$^-OOC{-}CH{=}CH{-}COO^- + 2OH^- \rightarrow {-}(C{\equiv}C{-}) + 2CO_2 + 2H_2O + 4e^- \tag{3}$$

$$\Delta_r G^0 \text{ (maleic)} = -18.2 \text{ Kcal/mol}$$
$$\Delta_r G^0 \text{ (fumaric)} = -13.8 \text{ Kcal/mol}$$

$$^-OOC{-}CH{=}CH{-}COO^- \rightarrow {-}(C{\equiv}C{-}) + 2CO + 2OH^- \tag{4}$$

(this is not an electrochemical reaction)

$$\Delta_r G^0 \text{ (maleic)} = +68.4 \text{ Kcal/mol}$$
$$\Delta_r G^0 \text{ (fumaric)} = +72.8 \text{ Kcal/mol}$$

$$^-OOC{-}CH{=}CH{-}COO^- \rightarrow {-}(CH{=}CH{-}) + 2CO_2 + 2e^- \tag{5}$$

$$\Delta_r G^0 \text{ (maleic)} = -4.0 \text{ Kcal/mol}$$
$$\Delta_r G^0 \text{ (fumaric)} = +0.4 \text{ Kcal/mol}$$
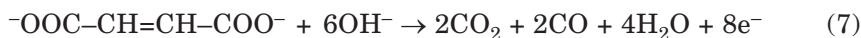
$$^-OOC{-}CH{=}CH{-}COO^- \rightarrow {-}(CH{=}CH{-}) + CO + O_2 + 2e^- \tag{6}$$
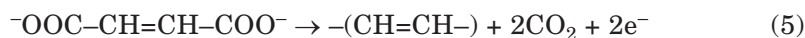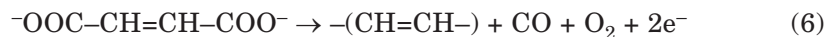
$$\Delta_r G^0 \text{ (maleic)} = +30.2 \text{ Kcal/mol}$$
$$\Delta_r G^0 \text{ (fumaric)} = +34.6 \text{ Kcal/mol}$$

$$^-OOC-CH=CH-COO^- + 6OH^- \rightarrow 2CO_2 + 2CO + 4H_2O + 8e^- \qquad (7)$$
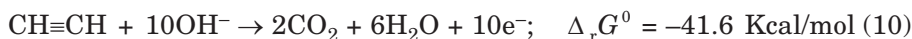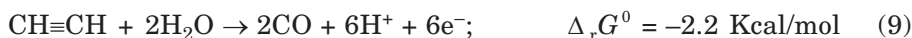
$$\Delta_r G^0 \text{ (maleic)} = -91.2 \text{ Kcal/mol}$$

$$\Delta_r G^0 \text{ (fumaric)} = -86.8 \text{ Kcal/mol}$$
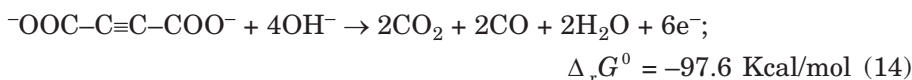
Other sources of CO and $CO_2$ may be:

$$CH\equiv CH + 6OH^- \rightarrow 2CO + 4H_2O + 6e^-; \qquad \Delta_r G^0 = -116.8 \text{ Kcal/mol (8)}$$
$$CH\equiv CH + 2H_2O \rightarrow 2CO + 6H^+ + 6e^-; \qquad \Delta_r G^0 = -2.2 \text{ Kcal/mol} \quad (9)$$
$$CH\equiv CH + 10OH^- \rightarrow 2CO_2 + 6H_2O + 10e^-; \quad \Delta_r G^0 = -41.6 \text{ Kcal/mol (10)}$$
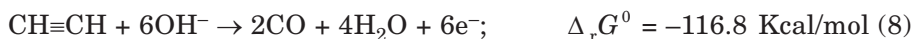
Also concurrent generation of oxygen at the electrode ($4OH^- \rightarrow O_2 + 4e^- + 2H_2O$) could contribute to the formation of CO and $CO_2$.

Whereas for acetylenedicarboxylic acid we have:

$$^-OOC-C\equiv C-COO^- \rightarrow -(C\equiv C-) + 2CO_2 + 2e^-; \qquad \Delta_r G^0 = -23.8 \text{ Kcal/mol} \quad (11)$$
$$^-OOC-C\equiv C-COO^- \rightarrow -(C\equiv C-) + 2CO + O_2 + 2e^-; \; \Delta_r G^0 = + 99.1 \text{ Kcal/mol (12)}$$
$$^-OOC-C\equiv C-COO^- + 2H_2O \rightarrow -(CH=CH-) + 2CO_2 + 2OH^- \qquad (13)$$
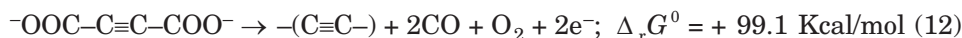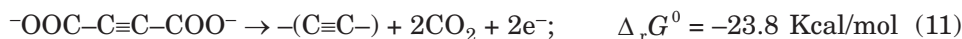
Reaction (13) is not an electrochemical reaction and cannot occur in our conditions.

$$^-OOC-C\equiv C-COO^- + 4OH^- \rightarrow 2CO_2 + 2CO + 2H_2O + 6e^-;$$

$$\Delta_r G^0 = -97.6 \text{ Kcal/mol (14)}$$
$$^-OOC-C\equiv C-COO^- + 2H_2O \rightarrow CH\equiv CH + 2CO_2 + 2OH^- \qquad (15)$$

Reaction (15) is not an electrochemical reaction and cannot occur in our conditions.

There are only two reactions (R.) that can produce acetylene from maleic and fumaric acid, R.(1) and R.(2). Based on $\Delta_r G^0$ only R.(1) is not so far from the equilibrium, whereas R.(2) is considerably less favoured from the thermodynamic standpoint. Thus, only R.(1) occurs to produce acetylene and $CO_2$. However, other secondary reactions occur, like formation of polyynes (which we have detected by FT-IR spectroscopy). Again, R.(3) is thermodynamically favoured over R.(4); moreover, R.(4) is not an electrochemical half-reaction and can be completely excluded in our conditions. Hence, polyynes are formed together with carbon dioxide according to R.(4) and not with CO. The formation of polyenes according to R.(5) and R.(6) is less favoured than the formation of polyynes (compare $\Delta_r G^0$ of R.(5) and R.(6) with R.(3)), but cannot be excluded at all. From the thermodynamic standpoint, the most probable source of carbon monoxide is from reaction R.(7), which

involves complete oxidation of maleic or fumaric acid with formation of carbon dioxide and monoxide. An alternative way that might lead to the production of CO could be the anodic oxidation of acetylene once it is formed from fumaric or maleic acid according R.(8)-R.(10).

As regards, acetylenedicarboxylic acid, its anodic oxidation should produce polyynes and $CO_2$, as shown by R.(11) in agreement with our experimental results. Also in this case, the reaction leading to polyynes and CO R.(12) is thermodynamically improbable. Thus, also in this case, the most reasonable source of CO is from the complete oxidation of acetylenedicarboxylic acid molecule R.(14).

Experimentally, there was no acetylene formation from electrooxidation of acetylenedicarboxylic acid and this is in agreement with theoretical expectations. In fact, R.(14) showing the formation of acetylene from acetylenedicarboxylic acid is not an electrochemical reaction and hence cannot occur at the anode. The same reasoning should be applied to R.(13), suggesting the simultaneous formation of polyenes and carbon dioxide. This reaction is not an electrochemical half-reaction either and cannot occur at the anode. Moreover, this reaction is a paradox, because it implies that original acetylenic carbon atoms should undergo a reduction from formal oxidation state of zero to –1 state during an electrooxidation.

The thermodynamic argument is simple and permits to rationalize the results of our investigation. Of course, a deeper analysis involving also the electrode kinetics and chemical species sorption on the electrodes might be needed for a complete understanding of the complex phenomenon studied.


## CONCLUSIONS

Acetylene, $CO_2$ and CO, detected qualitatively and quantitatively are the products of anodic oxidation of the dipotassium salts of maleic and fumaric acids. Best acetylene yields are achieved by using concentrated solutions and at a high current density of fumaric acids. Maleic acid favours the highest yields of $CO_2$.

Acetylenedicarboxylic acid gives only a mixture of $CO_2$ and CO as anodic gases.

Coupling reactions happen during the anodic oxidation of maleic and fumaric acids. This is suggested by the formation of brown products at the anode, which were studied by UV/VIS spectroscopy. The brown colour is due to conjugation along the chains of these products. The coupling reaction leads to the formation of polyynes rather than polyenes and this is also true of acetylenedicarboxylic acid.

The black products formed at the anode from fumaric acid and maleic acid studied by FT-IR spectroscopy show the presence of triple bonds, suggesting that acetylenic and also allenic carbyne-like products are formed during decarboxylation and coupling reactions at the anode.

Ten different reactions were studied to explain how maleic acid and fumaric acid produce acetylene, $CO_2$ and CO as well as polyynes. For all these reactions, the $\Delta_r G^0$ values were calculated. Acetylene and polyynes are always formed together with carbon dioxide; polyenes can be formed together with $CO_2$. The unique possible source of CO is from the complete oxidation of maleic or fumaric acid, because all the other possible reactions are thermodynamically unfavoured or are not electrochemical reactions. An alternative explanation of the CO formation involves the anodic oxidation of acetylene at the anode once it is formed from the precursor molecule.

Five different reactions have been considered to explain the formation of CO and $CO_2$ from acetylenedicarboxylic acid. A clear explanation of the fact that no acetylene production is observed is based on the fact that the reaction that should produce acetylene is not an electrochemical reaction and cannot occur at the anode. Thus, only polyynes and $CO_2$ are formed directly by electrooxydation of acetylenedicarboxylic acid. CO is formed by a secondary reaction involving the oxidation of the entire starting molecule.

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## SAŽETAK

### Novi pristup anodnoj dekarboksilaciji nezasićenih dikarboksilnih kiselina. 1. dio: fumarna, maleinska i etindikarboksilna kiselina

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Elektrokemijski su oksidirane dikalijeve soli maleinske, fumarne i etindikarboksilne kiseline, a produkti reakcija kvalitativno i kvantitativno su analizirani UV/VIS i FT-IR spektroskopijom. Produkti elektrooksidacije maleinske i fumarne kiseline jesu etin, ugljikov dioksid, ugljikov monoksid i poliini. Najveći prinos etina postignut je oksidacijom fumarne kiseline, a glavni produkt oksidacije maleinske kiseline bio je ugljikov dioksid. Kada je koncentracija reaktanata bila visoka, a gustoća struje velika, produkti oksidacije bili su ugljikovi spojevi koji sadrže karbine prepoznate po karakterističnim vibracijama trostrukih veza. Anodnom oksidacijom acetilendikarboksilne kiseline nastaje smjesa ugljikova dioksida, ugljikova monoksida i topljivih poliina, ali nije primjećen slobodni etin. Elektrokemijske oksidacije navedenih kiselina objašnjene su s pomoću 15 kemijskih reakcija i njihovih reakcijskih Gibbsovih energija.