ANODIC OXIDATION OF MALIC ACID

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Abstract

Malic anodic oxidation has been performed in a selective way leading to succinaldehyde (and derivatives). The oxidation mechanism (in galvanostatic conditions and partial neutralisation of the acid) has been established according to structural analysis of products by ^{1}H-NMR and GC-MS methods.

Introduction

Carboxylic acid anodic oxidation can be selectively directed towards one-or two-electron oxidation route by choosing the appropriate electrochemical conditions: platinum electrode, high current densities or graphite electrode, small current densities [1]. However, when the substrate does not have a special structure a mixture of products is usually obtained [2]. When the substrate has a structure that could stabilise a carbenium intermediate (e.g. contains a substituent with a + E effect, in α-position vs. carboxyl groups) the two-electron route is exclusively followed even in conditions which favour one-electron oxidation [3-5].

This paper shows the results of malic acid anodic oxidation. This compound has two type of carboxylic groups having different acidities. Early results concerning its oxidation [6-8] in aqueous solution showed an unselective oxidation process leading to destructive oxidation products (mixture of glioxylic, oxalic and formic acids).

Our aim was to perform a selective oxidation of malic acid according to a simple principle: when the substrate has carboxylic groups with different acidities, at a partial neutralisation only the most acidic carboxylic group will react, and then the entire process will follow the way opened by this initial oxidation.

Materials and Methods

The electrolyte was obtained by dissolution of 0.536 g malic acid in ~10 mL CH_3OH and partial neutralisation (10%) with CH_3ONa in CH_3OH (2.28 M).

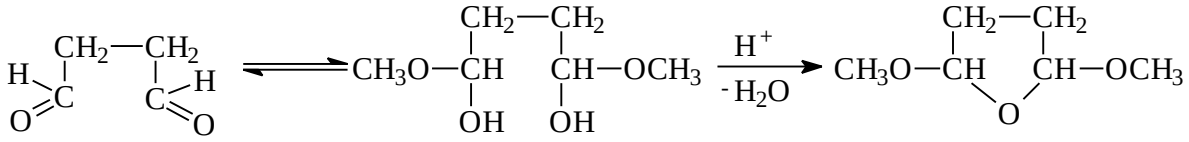
The anodic oxidation has been performed at constant current (80 mA/cm^2) in an undivided cell on platinum anode, at about 15^0C, using an amount of electricity equivalent to twice the theoretical value (6 F/mole). At the end of electrolyses the mixtures have been worked up in two different ways: (i) 5% of the total volume was kept for 2 hours on VIONIT-CS_3 high acid ion exchanger (in order to retain the Na salts), then analysed by GC-MS, and (ii) the left (95 %) mixture was treated with acidic dinitrophenylhydrazine (DNFH) solution in ethanol, then the precipitated dinitrophenylhydrazones were filtered, washed and analysed by ^{1}H-NMR.

GC-MS analyses were performed on a Varian 3400 Saturn 2 System gas chromatograph-mass spectrometer u*sin*g a 25 m DB 5 capillary glass column, and ^{1}H-NMR analyses on a 400 MHz Varian spectrometer.

Results and Discussion

Malic acid anodic oxidation has been done in conditions which favour one-electron oxidation (Kolbe reaction): platinum anode, high anodic current, small degree of neutralisation. These conditions could lead to the occurrence of two different ways of oxidation during the same electrolysis: a non-Kolbe process for the carboxyl group in α-position and a Kolbe process for the carboxyl group in β-position versus hydroxyl group. The former group is more acidic and will exist as carboxylate (in conditions of partial neutralisation), while the second will act further in agreement with the chosen electrochemical conditions favouring one-electron oxidation.

GC-MS analysis evidenced in the final electrolysis mixture only one main product 2,5-dimethoxytetrahydrofuran **5**, near ureacted malic acid. The formation of **5** can be explained by the acetalisation of the real electrolysis main product: the succindialdehyde during the work up (in CH_3OH solution in the presence of the high acid ion exchanger), according to *scheme 1*.



Scheme 1

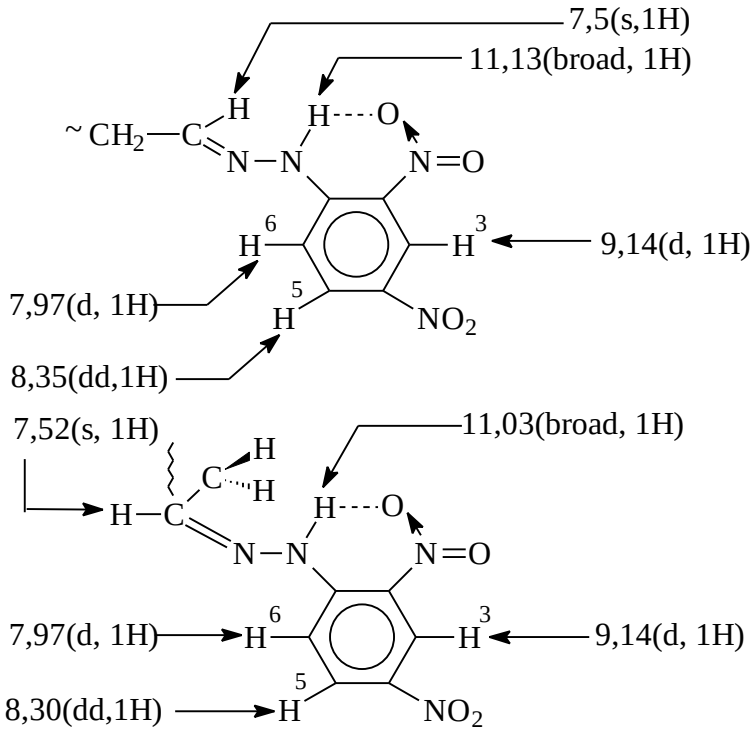
The mass spectrum of **5** is: 132(1.6) $C_6H_{12}O_3]^{\bullet+}$, M; 116 (8) $C_5H_8O_3]^{\bullet+}$; 85(2) $HCO\text{-}(CH_2)_2CO^+$; 75(100) $C_3H_7O_2^+$; 74(7) $C_3H_6O_2]^{\bullet+}$;58(3) $C_2H_2O_2^+$; 43(6) $C_2H_3O^+$; 31(9) $CH_2{=}^+OH$; 29(9) CHO^+.

The mass balance u*sin*g GC-MS result allowed the calculation of a 48 % yield.

^{1}H-NMR analysis shows the formation of a mixture of *sin* (40 %) and *anti* (60 %) stereoisomers of succindialdehyde-2,4-dinitrophenylhydrozones. *Scheme 2* shows the attributions of ^{1}H-NMR signals in agreement with their respective structures.

Their attributions are justified by the following arguments:

- H^3, H^5, and H^6 protons in the two stereoisomers have the coupling constants JH^3H^5 of 2 Hz and 2.4 Hz, and JH^5H^6 of 9.4 Hz and 9.3 Hz in *sin* and *anti* isomers, respectively.
- Characteristic chemical shifts for the -CH=N- proton (7.52 ppm and 7.00 ppm in *sin* and *anti* isomers, respectively) are associated to a very weak (less then 1 Hz) coupling constant with CH_2 vicinal proton (the corresponding chemical shifts for this type of protons found in data tables [9] are 6.1 - 7.7 ppm, with the mention that *sin* protons appear more deshielded than *anti* protons; for the coupling constant with vicinal alkyl groups values between 0 and 3 Hz are mentioned [9].
- The chemical shifts for NH protons are different in the two isomers (11.03 and 11.13 ppm in *sin* and *anti*, respectively). This interesting difference could illustrate a different tendency to form intramolecular hydrogen bonds with the nitro group (which is sterically unfavoured in *sin* isomer).
- H^5 protons show chemical shifts of 8.30 and 8.35 ppm (they can be easily identified in 400 MHz ^{1}H-NMR spectrum); their integrals are in agreement with the 40/60 ratio previously mentioned. Even if it is more difficult to be explained, this small difference in the chemical shifts could be the result of the same phenomenon of diminution of the tendency to form hydrogen bonds in the *sin* vs. *anti* isomer, that is consequently followed by a different electronic effect in the *para* position vs. nitro group.

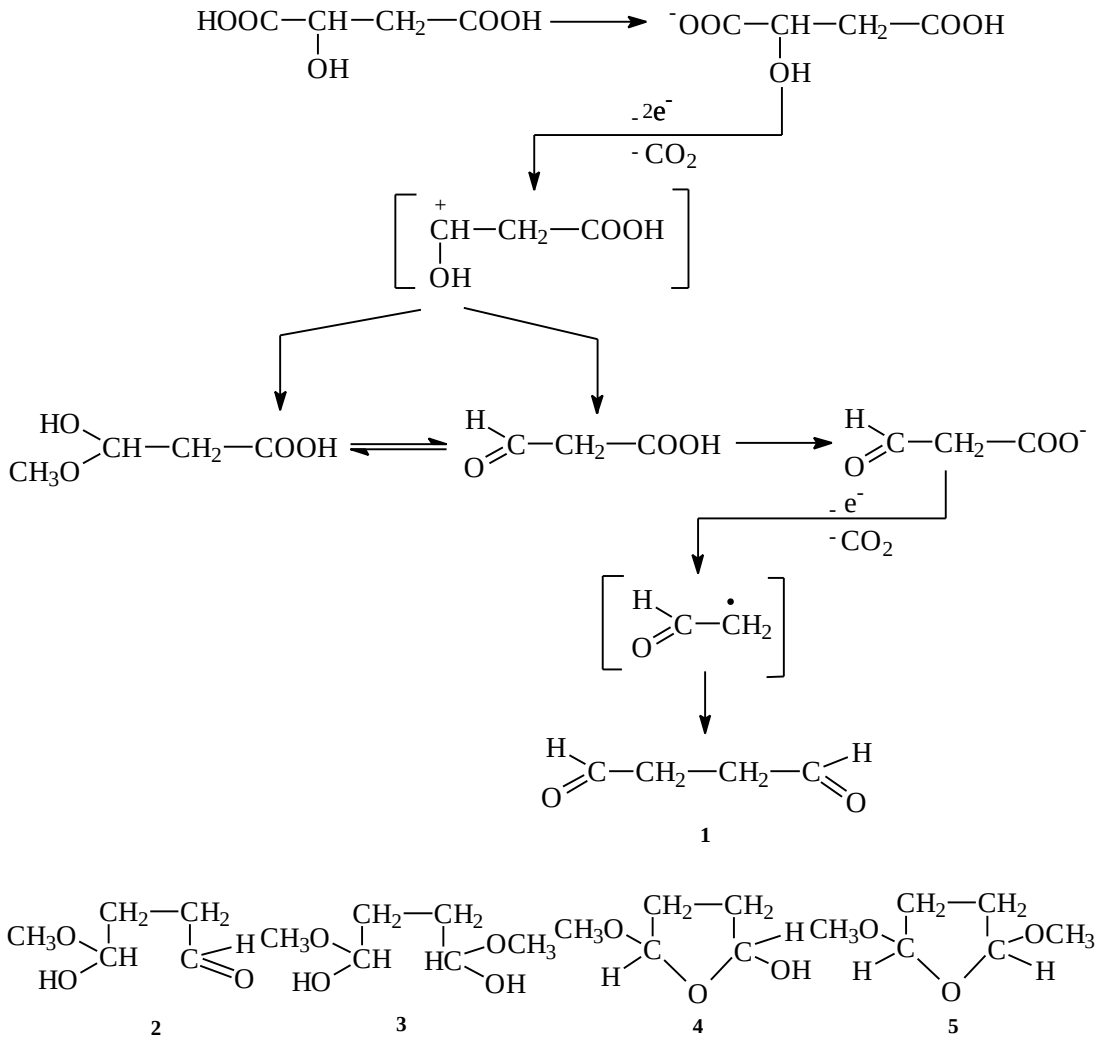


Scheme 2

Analysis of the ^{1}H-NMR spectrum allowed to calculate a total yield of 56 % for the succindialdehyde isomeric dinitrophenylhydrazones. This result shows that the final electrolysis mixture contains more compounds which are succindialdehyde derivatives than those resulted by GC-MS analysis. Taking into account the conversion (76 %) we can estimate a selectivity in succindialdehyde derivatives (halfacetals, acetals) of 74 %.

Detailed examination of ^{1}H-NMR and GC-MS analyses allowed to formulate the mechanism for malic acid anodic oxidation.*Scheme 3* shows in the first step the oxidation of the higher acidic carboxylic group (that is the only one in carboxylate form in conditions of partial neutralisation). As this carboxylic group is in α-position vs. hydroxyl group a two-electron oxidation occurs leading to the formation of the non-Kolbe product: malonic halfaldehyde halfacetal (**2**), no matter what electrolysis parameters are. **2** is the most acidic compound in the system now and will be consequently oxidized further. Its structure, as well as the imposed electrochemical parameters, are adequate to follow a further one-electron (Kolbe) oxidation leading especially to the dimeric product. This dimer exists in different half acetalic forms with open or cyclic structures (**1**-**5**). Due to the local acidity generated by the non-Kolbe cationic mechanism other compounds of type **4** or even **5** could result. The small occurrence of a β-aldehydic acid decarboxylation (in comparison with the similar phenomenon noticed in the case of citric acid anodic oxidation [10]) is probably the

consequence of the weak concentration of free aldehydic acid.



Scheme 3

Conclusion

Study of malic anodic oxidation proved the possibility to perform a selective anodic oxidation of the higher acidic carboxylic group. It confirms the result obtained in citric acid anodic oxidation. In the case of malic acid a double selectivity can be attained in conditions favouring a Kolbe mechanism: non-Kolbe oxidation (i) of the carboxyl group in α-position leading to malonic half aldehyde, that becomes the most acidic species in the system and is successively oxidised in a Kolbe mechanism (ii).

The succinaldehyde (as well as its derivatives formed by reactions with the solvent) results with a satisfactory selectivity. Even if the process has not been optimised, the 70 % selectivity recommends this reaction as a prospective preparatory method. In comparison with

the already known electrochemical preparatory method (by electrolysis of formylacetic acetal potassium salt), a procedure based on our results has evident advantages due to the fact that it is more direct and uses a more accessible raw material.

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