ELECTROCHEMICAL REDUCTION OF MALEIC AND FUMARIC ACIDS AND THEIR DIMETHYL ESTERS IN METHANOL AT A MERCURY ELECTRODE

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The electrochemical reduction of maleic and fumaric acids and their dimethyl esters have been investigated by cyclic voltammetry on HMDE in pure methanol. The cyclic voltammograms of the free acids show two successive reduction waves due to the influence of the different strength of the carboxylic groups on the double bond reduction. The reduction mechanism is verified by examining the effect of different supporting electrolytes, proton donors, and strong bases on the reduction waves. The double bond reduction of the corresponding dimethyl esters takes place in one step.

The electrochemical behaviour of fumaric (FA), maleic (MA) acids and their derivatives has intensively been studied in aqueous solutions during the last 50 years[1-7]. In aqueous buffered solutions, the buffer capacity and the ionic strength of the solution strongly affect the reduction wave of FA, MA and their diethyl esters[8]. In acid solutions the protonated forms of FA and MA give kinetic waves which are more positive than the corresponding waves of undissociated acids[9-11]. The reduction product of both acids in all cases has been proved to be succinic acid. Different products have been obtained in the case of substituent acids. Chloro derivatives give, depending on pH, chlorosuccinic or succinic acid[12], while dihydroxyfumaric acid (DHF) is reduced only in strong acid solutions to tartaric acid[13].

Little attention seems to have been paid to the study of the above compounds in non-aqueous media. In aprotic solvents the influence of low temperatures on the rate of dimerisation of the initial anionic radical of diethyl fumarate has been studied[14].

In a previous work the electrochemical behaviour of DHF has been investigated in methanolic solutions, where an entirely different reduction mechanism than that in aqueous media has been proposed[15]. As an extension of that study, the present work deals with electroreduction of FA, MA and their dimethyl esters in pure methanol. The effect of different supporting electrolytes, proton donors, and proton acceptors on the reduction waves is examined in order to clarify the reduction mechanism. The reduction mechanism of each substance is also discussed.

EXPERIMENTAL

Cyclic voltammetric *i–E* curves were carried out on a HMDE (PAR 9323) with a surface area of $3 \cdot 51 \cdot 10^{-2}$ cm^2. The experimental set-up included a G. Bank Elektronik PCA-72 L potentiostat; a G. Bank Elektronik VSG-72 L function generator and a Hewlett Packard 7045 X–Y recorder. D.c. polarograms were taken with a Polariter PO4 of Radiometer.

All potential values are refferred to the aqueous calomel electrode (SCE) saturated with NaCl. A Pt sheet has been used as counter electrode. Both counter and reference electrodes were separated from the working electrode compartment by glassy diaphragms.

FA and MA as well as dimethyl maleate and dimethyl fumarate were from Fluka A.G. (Switzerland), *p.a.*, and were used as received. The other reagents used were methanol absolute und acetonfrei *p.a.* from Fluka, tetraethylammonium perchlorate *per polarografia* from Carlo Erba after removal of its humidity, lithium hydroxide (LAB) from Merck, lithium perchlorate *p.a.* tetrabutylammonium iodide *p.a.*, toluo-4-sulfonic acid *p.a.* and butyric acid *p.a.* all reagents from Fluka. A stock solution of CH$_3$ONa was prepared by dissolving Na in absolute methanol.

High purity Ar was used for oxygen removal and all measurements were taken in an Ar atmosphere. The experiments were carried out at $25 \pm 0 \cdot 1°$C.

RESULTS AND DISCUSSION

Fumaric Acid

Cyclic voltammograms of FA in methanolic solution on a HMDE are given in Fig. 1. It can be seen that FA is reduced in two successive irreversible waves, which are
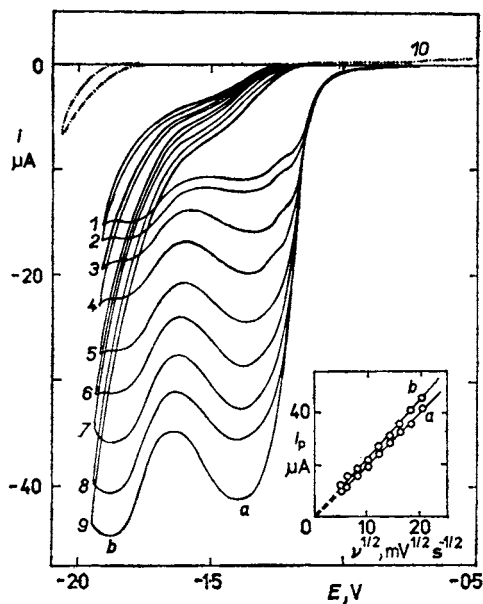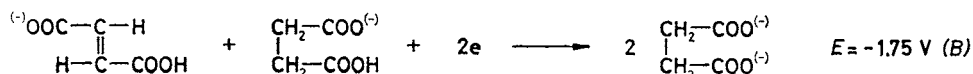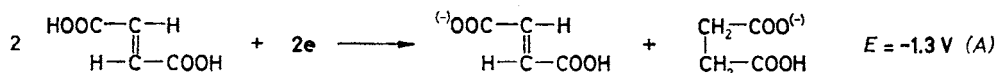

FIG. 1

Cyclic voltammograms of $2 \cdot 5 \cdot 10^{-3}$ mol l^{-1} FA in CH$_3$OH + 0·1 mol l^{-1} LiClO$_4$ at different scan rates (mV s^{-1}): *1* 25; *2* 36; *3* 64; *4* 100; *5* 144; *6* 196; *7* 256; *8* 324; *9* 400. Insert: Plot of i_p vs $v^{1/2}$ for the two reduction waves *a* and *b*. *10* Supporting electrolyte ($v = 100$ mV s^{-1})
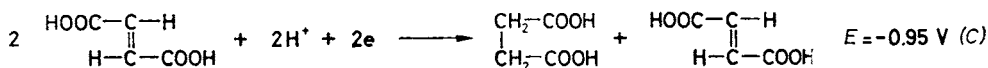
diffusion controlled, since the i_p is proportional to $v^{1/2}$ (insert in Fig. 1) and to the bulk concentration. There are two possible interpretations which can describe the appearance of these two waves. One of these could be the successive deposition of FA protons at different negative potentials, due to the different dissociation constants of the two carboxylic groups, as occurs in the case of dihydroxyfumaric acid[15]. The second interpretation could be double-bond reduction as it happens in aqueous solutions. The two-step reduction, in this case, can be explained by the catalytic effect of protons of the first FA dissociation. As has been proved in the case of nitro compounds[16] and azo compounds[17], the addition of an equivalent quantity of protons in CH_3OH results in the appearance of a pre-wave. This pre-wave is one quarter or one half of the whole wave in the case of a four-electron or a two-electron reduction, respectively. In our case, half the amount of FA could be reduced at -1.3 V, using the protons of the first dissociation and the remaining half of FA, as mono-anions, could be reduced at -1.75 V consuming the protons of the second dissociation according to the reactions:

$$2 \; \begin{array}{l} \text{HOOC}-\text{C}-\text{H} \\ \quad\quad \| \\ \text{H}-\text{C}-\text{COOH} \end{array} + 2e \longrightarrow \begin{array}{l} {}^{(-)}\text{OOC}-\text{C}-\text{H} \\ \quad\quad\quad \| \\ \text{H}-\text{C}-\text{COOH} \end{array} + \begin{array}{l} \text{CH}_2-\text{COO}^{(-)} \\ | \\ \text{CH}_2-\text{COOH} \end{array} \quad E = -1.3 \text{ V} \;\; (A)$$

$$\begin{array}{l} {}^{(-)}\text{OOC}-\text{C}-\text{H} \\ \quad\quad\quad \| \\ \text{H}-\text{C}-\text{COOH} \end{array} + \begin{array}{l} \text{CH}_2-\text{COO}^{(-)} \\ | \\ \text{CH}_2-\text{COOH} \end{array} + 2e \longrightarrow 2 \; \begin{array}{l} \text{CH}_2-\text{COO}^{(-)} \\ | \\ \text{CH}_2-\text{COO}^{(-)} \end{array} \quad E = -1.75 \text{ V} \;\; (B)$$
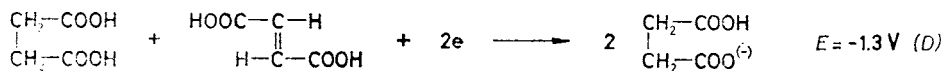
In order to distinguish which of the above two mechanisms takes place, the effect of strong acids and bases on the cathodic waves of FA was studied.

Reduction of Fumaric Acid in the Presence of Proton Donors

In Fig. 2 the hydrogen deposition of p-toluenesulfonic acid (p-TS) as well as the influence of this acid on the reduction waves of FA in CH_3OH is shown. When equimolar quantity of p-TS is added to a FA solution a pre-wave at less negative potentials appears (Fig. 2, curve 3). This behaviour can be explained assuming that p-TS is a strong acid in CH_3OH and its protons facilitate the double bond reduction, according to the following reactions:

$$2 \; \begin{array}{l} \text{HOOC}-\text{C}-\text{H} \\ \quad\quad \| \\ \text{H}-\text{C}-\text{COOH} \end{array} + 2\text{H}^+ + 2e \longrightarrow \begin{array}{l} \text{CH}_2-\text{COOH} \\ | \\ \text{CH}_2-\text{COOH} \end{array} + \begin{array}{l} \text{HOOC}-\text{C}-\text{H} \\ \quad\quad \| \\ \text{H}-\text{C}-\text{COOH} \end{array} \quad E = -0.95 \text{ V} \;\; (C)$$

As the added quantity of protons has been consumed the remaining half amount of FA is reduced at -1.3 V:

$$\begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix} \quad + \quad \begin{matrix} HOOC-C-H \\ \| \\ H-C-COOH \end{matrix} \quad + \quad 2e \quad \longrightarrow \quad 2 \begin{matrix} CH_2-COOH \\ | \\ CH_2-COO^{(-)} \end{matrix} \qquad E = -1.3\,V \;\; (D)$$

When the molar ratio of p-TS is 2 : 1 the whole quantity of FA is reduced in one step to succinic acid (SA) at -0.95 V (curve 4). The obscure wave at about -1.8 V is due to the hydrogen ions deposition of the reduction product, *i.e.* SA, and can be compared with curve 5 which represents the reduction wave of an authentic solution of SA.

With increasing p-TS concentration, the two waves of curve 4 (Fig. 2) remain unaffected and only the hydrogen deposition of the p-TS excess appears.

If the reduction waves of FA were due to the successive deposition of its protons then the hydrogen ions deposition of the added p-TS would superimpose on the reduction waves of FA. The cyclic voltammogram obtained in that case would be the sum of curves 1 and 2 of Fig. 2.

The first reduction wave of FA is distorted at low sweep rates, up to $100\ mV\ s^{-1}$, and a shoulder-like post-wave appears, as can be seen in Fig. 1 (curves 1 − 4). This peculiar behaviour could be explained by the different strength of FA and SA in CH_3OH. Assuming that in methanolic solutions FA is relatively stronger than SA, as happens in aqueous solutions $(pK_1 = 3.02$ for FA and $pK_1 = 4.16$ for SA), reaction (A) can be written as follows:

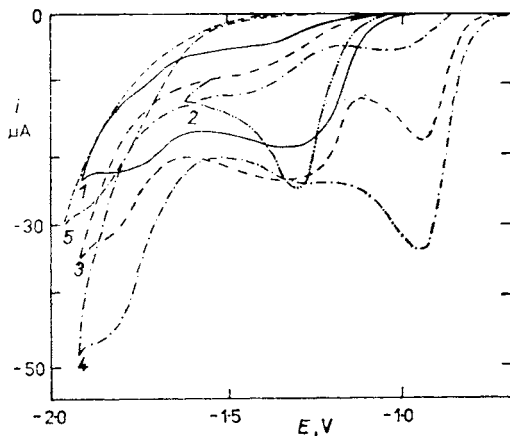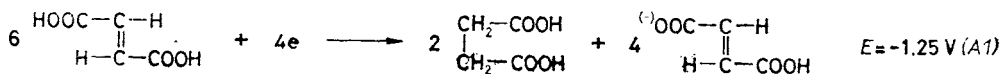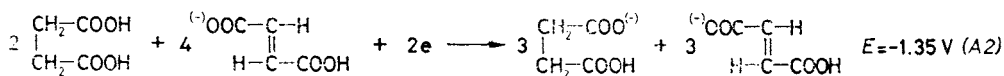$$6 \begin{matrix} HOOC-C-H \\ \| \\ H-C-COOH \end{matrix} \quad + \quad 4e \quad \longrightarrow \quad 2 \begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix} \quad + \quad 4 \begin{matrix} ^{(-)}OOC-C-H \\ \| \\ H-C-COOH \end{matrix} \qquad E = -1.25\,V\;(A1)$$

Fig. 2

Cyclic voltammograms of (concentrations in mol l^{-1}): 1 $2.5 . 10^{-3}$ FA; 2 $2.5 . 10^{-3}$ p-TS; 3 $2.5 . 10^{-3}$ FA + $2.5 . 10^{-3}$ p-TS; 4 $2.5 . 10^{-3}$ FA + $5 . 10^{-3}$ p-TS; 5 $2.5 . 10^{-3}$ SA. $100\ mV\ s^{-1}$

and

$$E = -1.35 \text{ V } (A2)$$

The above mechanism suggests that the relative heights of the curves I_a and I_b should be 2 : 1 (Fig. 3). Furthermore, according to reaction (D) or $(A2)$, FA should be reduced in one step in the presence of equimolar quantity of SA, as indeed happens (curve 3, Fig. 3). The second peak of curve 3 is due to the hydrogen ions deposition of monosuccinate — see Eq. (D) — and can be compared with curve 2, which represents the reduction of succinic acid monoanions.

Reduction of Fumaric Acid in the Presence of Strong Bases

As Fig. 4 shows, equimolar quantity of base decreases in half the height of both reduction waves, while a new peak appears at more negative potentials (curve 2). The simultaneous decrease of both waves suggests that the dissociation of the two stages of FA in CH_3OH overlap appreciably, so that the two dissociation equilibria of the acid still exist, since the methanolic solution is unbuffered. These equilibria could be affected by the addition of an acid with a pK-value lying between the two pK-values of FA. So, the presence of equimolar quantity of SA in the methanolic solution of FA/LiOH (molar ratio 1 : 1) shifts the equilibrium to the undissociated monoanionic form of FA. In this case, this reduction takes place according to Scheme 1:
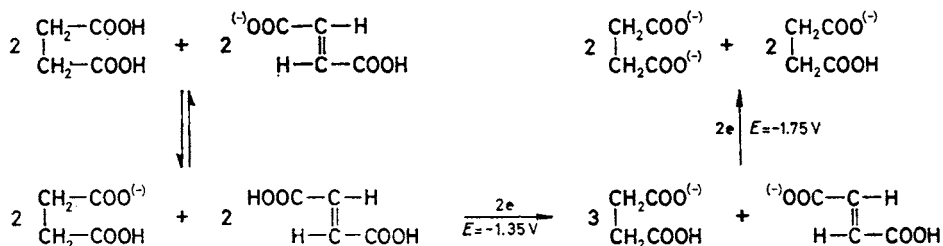
SCHEME 1

The above mechanism suggests that the FA monoanions in the presence of an equimolar quantity of SA are reduced in two steps (curve 4 of Fig. 4).

The wave at $-2 \cdot 1$ V, as well as the unique cathodic wave when 2 moles base *per* 1 mol depolarizer are present in the solution are due to the reduction of FA dianions consuming the protons of CH_3OH. The CH_3O^- ions formed on the electrode

surface during the reduction of FA dianions cause anodic dissolution of the mercury resulting in the appearance of a couple of peaks at positive potentials[18].
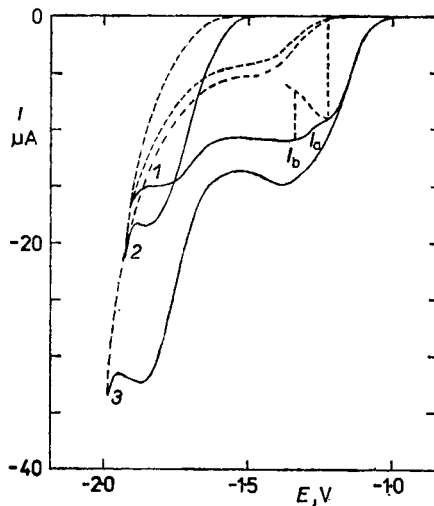
FIG. 3

Cyclic voltammograms of (concentrations in mol l^{-1}): *1* 2·5 . 10^{-3} FA; *2* 5 . 10^{-3} SA + 2·5 . 10^{-3} LiOH; *3* 2·5 . 10^{-3} FA + 2·5 . . 10^{-3} SA. 25 mV s^{-1}
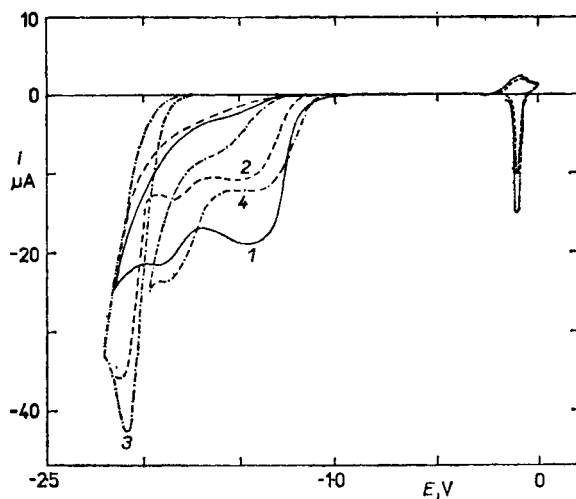
FIG. 4

Cyclic voltammograms of *1* 5 . 10^{-3} mol l^{-1} FA and a mixture of FA and LiOH at different molar ratios: *2* 1 : 1; *3* 1 : 2; *4* 5 . 10^{-3} mol l^{-1} FA + 5 . 10^{-3} mol l^{-1} LiOH + 5 . 10^{-3} mol . . l^{-1} SA. 100 mV s^{-1}

Maleic Acid

The cyclic voltammogram of MA in CH_3OH exhibits also two diffusion controlled reduction waves which are strongly dependent on the nature of the supporting electrolyte (Fig. 5). When $(C_4H_9)_4NI$ is used two well formed waves appear with a height ratio of about 1 : 2 under steady state or polarographic conditions. In the presence of $(C_2H_5)_4N^+$ ions a small pre-wave at less negative potentials appears with a simultaneous decrease of the height of both waves. When Li^+ ions are used the height of the pre-wave is almost equal to that of the first wave while the height of the second one becomes even smaller.

From Figs 1 and 5 it can easily be concluded that the reduction mechanism of MA in CH_3OH must be different from that of FA. The cyclic voltammetric differentiation of the two depolarizers must be attributed to the different dissociation constants of the two acids. Assuming again that the first dissociation constant of MA in CH_3OH is greater, and the second one smaller as compared with FA, and taking into account the height ratio of the two waves, the following mechanism could be proposed:
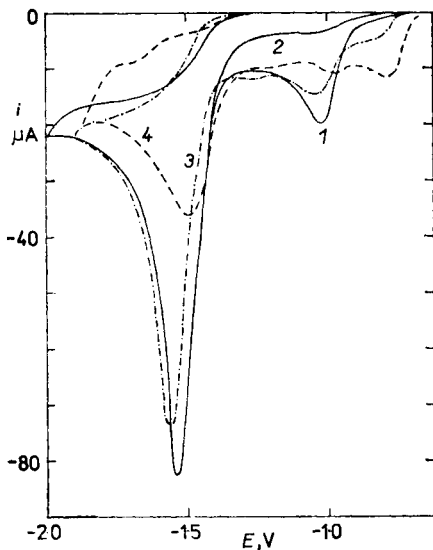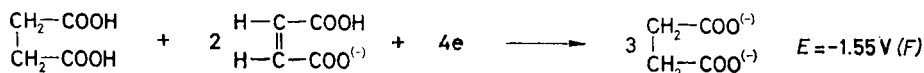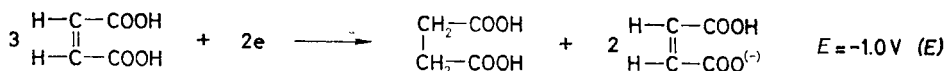
$$3 \; \begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix} \; + \; 2e \; \longrightarrow \; \begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix} \; + \; 2 \begin{matrix} H-C-COOH \\ \| \\ H-C-COO^{(-)} \end{matrix} \quad E=-1.0\,V \;\; (E)$$

$$\begin{matrix} CH_2-COOH \\ | \\ CH_2-COOH \end{matrix} \; + \; 2 \begin{matrix} H-C-COOH \\ \| \\ H-C-COO^{(-)} \end{matrix} \; + \; 4e \; \longrightarrow \; 3 \begin{matrix} CH_2-COO^{(-)} \\ | \\ CH_2-COO^{(-)} \end{matrix} \quad E=-1.55\,V \;\; (F)$$

FIG. 5

Cyclic voltammograms of $2 \cdot 5 \cdot 10^{-3}$ mol . l^{-1} MA in different supporting electrolytes ($c = 0 \cdot 1$ mol l^{-1}): *1* $(C_4H_9)_4NI$, first cycle; *2* $(C_4H_9)_4NI$, second cycle; *3* $(C_2H_5)_4$. $NClO_4$; *4* $LiClO_4$. 100 mV s^{-1}

The above mechanism indicates that one third of the amount of the acid is reduced at -1.0 V and the remaining two thirds as monoanions are reduced at -1.55 V.

Furthermore, the succinic acid dianions formed at the electrode surface during the first cycle react with the MA molecules diffusing from the bulk giving MA monoanions. So, during the second cycle only one wave is developed at -1.55 V (Fig. 5, curve 2).

In order to support the above mechanism the effect of strong acids and bases on the reduction waves of MA was studied.

Reduction of Maleic Acid in the Presence of Proton Donors

In Fig. 6 the effect of *p*-TS on the reduction waves of MA is shown. When the molar ratio of the two acids in the solution is 1 : 1 the first reduction wave is increased at the expense of the second one while a pre-wave at less negative potentials appears. When the concentration of *p*-TS is troice that of MA, then the whole quantity of MA is reduced at the corresponding potential of the first wave with a simultaneous
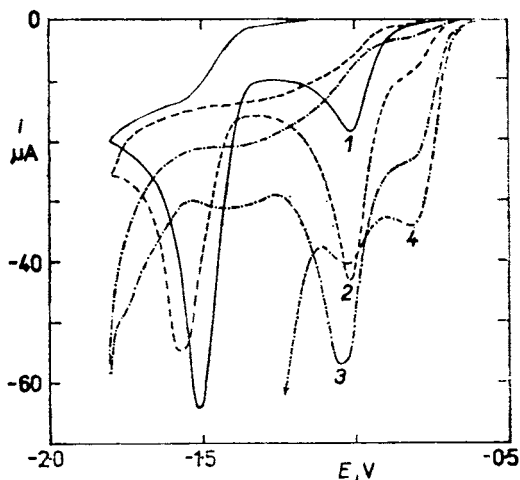

FIG. 6

Cyclic voltammograms of *1* $2.5 \cdot 10^{-3}$ mol. $. 1^{-1}$ MA in $CH_3OH + (C_4H_9)_4NI$ 0.1 mol. $. 1^{-1}$ and a mixture of MA and *p*-TS at different molar ratios: *2* 1 : 1; *3* 1 : 2; *4* 1 : 3. 50 mV s^{-1}
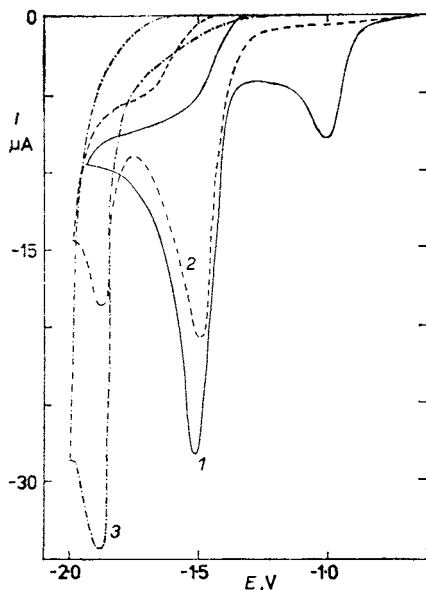
FIG. 7

Cyclic voltammograms of *1* $2.5 \cdot 10^{-3}$ mol. $. 1^{-1}$ MA in $CH_3OH + (C_4H_9)_4NI$ 0.1 mol. $. 1^{-1}$ and a mixture of MA and LiOH at different molar ratios: *2* 1 : 1; *3* 1 : 3. 100 mV s^{-1}

increase of the pre-wave (curve *3*). This pre-wave could be attributed to the formation of the MA protonated form as has been proved in the case of strong acid aqueous solutions[7,9-11,19].

When the concentration of *p*-TS is increased the equilibrium is shifted towards the protonated form, resulting in the enhancement of the pre-wave (curve *4*). The same mechanism could be accepted to be valid in the presence of Li^+ ions in CH_3OH. In this case the ion-pair between MA and Li^+ facilitates the double bond reduction and the pre-wave is developed at the same potential as in the case of H^+ ions, as can be concluded from Figs 5 and 6. The ion-pair formation between Li^+ and other depolarizers has also been proposed in other organic solvents[20].

Reduction of Maleic Acid in the Presence of Strong Bases

When an equimolar quantity of a strong base (CH_3ONa or $LiOH$) is added to the MA solution the first reduction wave disappears, while a new one emerges at more negative potentials (-1.9 V) (Fig. 7). Double quantity of base in the solution results in the appearance of only one wave at -1.9 V. The above behaviour suggests that the two dissociation constants of MA in CH_3OH differ essentially. So, the addition of the base causes consecutive neutralization of the two carboxylic groups.

From the above experimental results it is concluded that MA can be reduced from methanolic solutions in four different ways depending on the presence of the predominant form of the acid in the solution. The protonated form is reduced at -0.75 V, the undissociated MA at -1.0 V, the monoanions at -1.55 V, and the dianion form at -1.9 V.

Dimethyl Esters of Maleic and Fumaric Acids

The reduction of dimethyl maleate and dimethyl fumarate takes place in one irreversible diffusion-controlled wave at -1.275 and -1.15 V, respectively. The small difference between the two $E_{1/2}$'s suggests that the *cis–trans* configuration very little affects the double bond reduction of the above esters in CH_3OH. The obtained single cathodic wave corresponds to double bond reduction consuming the protons of CH_3OH, as during the reduction of the dianionic form of the acids.

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