

CYCLIC VOLTAMMETRIC AND GALVANOSTATIC ELECTROLYSIS STUDIES ON THE REDUCTION OF MALEIC ACID IN BUFFERED AND UNBUFFERED SOLUTIONS

S S VAGHELA, A D JETHVA, M S GOHIL, G RAMACHANDRAIAH^{*} P K GHOSH AND D VASUDEVAN^{**}

*Reactive Polymers Division, Central Salt and Marine Chemicals Research Institute
Gijubhai Badheka Marg, Bhavanagar 364 002. Gujarat. INDIA*

***Central Electrochemical Research Institute, Karaikudi 630 006.INDIA*

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Maleic acid (MA) is reduced in a two electron diffusion limited, irreversible step to succinic acid at a HMDE in buffered media at pH ≤ 8.5 . Galvanostatic reduction of MA in 0.53 M H_2SO_4 and 0.1 M Na_2SO_4 (pH 8.1) in an undivided cell yielded succinic acid (SA) in high yields. The product has been characterized by FTIR and 1H -NMR. Based on the results obtained, a plausible mechanism of reduction of MA has been suggested in various media.

Keywords: Maleic acid, cyclic voltammetry, galvanostatic electrolysis, product analysis, mechanism.

INTRODUCTION

Succinic acid can be obtained by the reduction of maleic acid or maleic anhydride [1]. The electrolytic reduction of maleic acid at different cathodes in sulfuric acid, benzene sulphonic acid or hydrochloric acid as supporting electrolytes [2-6] has been reported. Kanakam et al. [7] have investigated the reduction of maleic acid by polarography in the presence and the absence of different supporting electrolytes. However, the mechanism of electroreduction of maleic acid at different pH values has not been completely established.

The present paper describes the cyclic voltammetric behaviour of maleic acid in buffered media in an undivided cell. The product was characterized by FTIR and 1H -NMR.

EXPERIMENTAL

Reagents

High purity maleic acid (S.D. Fine Chemicals Ltd, India) was used as received. All other chemicals used in this study were of AR grade. All solutions were prepared in doubly distilled water.

Cyclic voltammetry

Cyclic voltammetric measurements were carried out using a conventional three electrode cell with

parts for introducing the working, reference and counter electrodes. HMDE (0.017 cm^2), SCE and platinum wire served as the working, reference and counter electrodes respectively. Solutions containing 1 M H_2SO_4 , 0.05 M H_2SO_4 , 0.1 M CH_3COONa and 0.1 M KH_2PO_4 in 0.1 M Na_2SO_4 were used as supporting electrolytes. The pH of the solution in the case of 0.1 M CH_3COONa and 0.1 M Na_2SO_4 mixture was adjusted to the desired value between 1 to 5.5 with 1:1 H_2SO_4 solution while that of 0.1 M KH_2PO_4 and 0.1 M Na_2SO_4 mixture was adjusted to the value between 6 to 8.5 with NaOH solution.

Galvanostatic electrolysis and product analysis

A 30 ml solution of 1 g maleic acid (8×10^{-3} moles) was reduced electrolytically at a Hg pool cathode (area 12.56 cm^2) against a platinum gauze anode in a single compartment cell. A solution containing 0.1 M H_2SO_4 (pH 0.81) and 0.1 M Na_2SO_4 (pH 8.1) were used as supporting electrolytes to obtain the product as succinic acid and its disodium salt, respectively. Electrolysis was carried out in each case at 40 mA.cm^{-2} till a charge equivalent to $2F$ was passed. The percentage of product formed at the end of electrolysis was analyzed with the help of relative intensities of 1H -NMR peaks in D_2O at $\delta = 6.38 \text{ ppm}$ and 5.91 ppm corresponding to $-CH=CH-$ group of maleic acid and its sodium salt

^{*} Author for correspondence

and 2.44 ppm and 2.18 ppm for $-\text{CH}_2-\text{CH}_2-$ group of those of the products respectively [8].

Instrumentation

Cyclic voltammograms were recorded with EG and G PAR models 175 Universal Programmer and 174 A Polarographic analyzer coupled with a three electrode assembly EG & G PAR model 303 SMDE/HMDE [9]. An Aplab D.C. Power supply (L 1288SR) was employed for galvanostatic electrolysis.

The $^1\text{H-NMR}$ spectra of the electrolyzed solution were recorded using Bruker Avance DPX-200-FT NMR-200 MHz spectrometer and IR spectra recorded using a Perkin Elmer Spectrometer (GX FTIR system).

RESULTS AND DISCUSSION

Cyclic voltammetric response observed for the reduction of 1 mM maleic acid in 1 M H_2SO_4 at different scan rates (0.02 to 0.50 V/s) is shown in Fig. 1. A single cathodic peak is observed with no corresponding anodic peak. A slight shift in the peak potential is observed with increase in sweep rate. The $i_p - v^{1/2}$ plot is a straight line passing through the origin (Fig. 1B). The above results indicate a diffusion controlled irreversible reduction of MA under the present experimental conditions.

The effect of pH on the cyclic voltammetric response of MA in buffered media is shown in Fig. 2A. E_p is shifted cathodically with the increase in pH and a slight decrease in peak current (i_p) is observed with increase in pH. In the pH range of 2.5 to 4.5, the single peak is split into two at low scan rates ($\leq 0.2 \text{ Vs}^{-1}$). The E_p -pH plot shown in Fig. 2B is linear.

The i_{pc} and $E_{p/2}$ data measured at three different scan rates and pH pertinent to Fig. 2A are summarized in Table I. The i_{pc} value at a given scan rate was large at pH = 0 and decreases with increase in the pH.

Cathodic shift of E_p with pH indicates proton participation in the reaction. A slight decrease in the peak current with increase in the pH is observed. This is due to a decrease in the diffusion coefficient of the medium due to increase in its viscosity.

It is noted from the data in Table I that at all scan rates the $E_{p/2} - E_p$ values lie in the range of 23 to 39 mV in 1 M H_2SO_4 as well as in buffer solutions at pH = 0 to 1.5. But it increased to 55

to 87 mV in the pH ranges 1.5 to 3 and 5 to 8.1. The reasons are discussed later in the text. In the pH range 3 to 4.5 the single peak splits into two peaks.

Galvanostatic electrolysis and product analysis

The electrolyzed solution after theoretical time of galvanostatic electrolysis was subjected to spectral studies. The $^1\text{H-NMR}$ spectra of the electrolyzed solution after electrolysis indicated 100% succinic acid and 99.6% sodium succinate in 0.1 M H_2SO_4 (pH = 0.81) and 0.1 M Na_2SO_4 (pH 8.1) media respectively. The yields presented here are based on NMR and not the actual isolated yields. The product showed a single peak in the $^1\text{H-NMR}$ at $\delta = 2.44$ ppm which corresponds to the two symmetric methylene ($-\text{CH}_2$) protons. A strong absorption band at 1695 cm^{-1} was observed in the FTIR spectra of the product corresponding to $>\text{C}=\text{O}$ stretch apart from other absorptions.

The product from 0.1 M Na_2SO_4 showed a peak at $\delta = 2.18$ in $^1\text{H-NMR}$ spectra and a broad band at 1563 cm^{-1} for $>\text{C}=\text{O}$ stretch, in the FTIR spectra, corresponding to the disodium salt of succinic acid. The $^1\text{H-NMR}$ peaks at $\delta = 6.38$ or 5.91 in the acid or neutral media and the strong band at 1637 cm^{-1} in the FTIR spectra of maleic

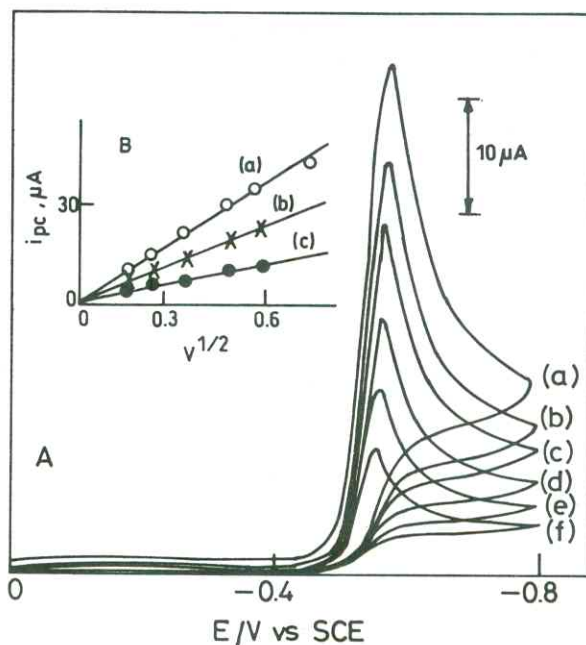


Fig. 1: (A) Cyclic voltammetric responses of 1 mM maleic acid at HMDE in 1 M H_2SO_4 . Scan rate (V/s) (a) 0.50 (b) 0.30 (c) 0.20 (d) 0.10 (e) 0.05 (f) 0.02 (B) Plot of i_p vs square root of scan rate pH (a) 0 (b) 5 (c) 8.1

acid (or its disodium salt) were absent in those for the electrolyzed product.

The products from the electrolyzed solutions stated above were isolated and characterized

- the compound obtained from 0.1 M H₂SO₄ showed a peak at $\delta = 2.44$ ppm that corresponds to the protons of two symmetric methylene (-CH₂) groups in ¹H-NMR and a strong absorption band at 1695 cm⁻¹ corresponding to >C=O stretch, apart from other bands in FTIR spectra for succinic acid.
- the product obtained from 0.1 M Na₂SO₄ showed a peak at $\delta = 2.18$ ppm in ¹H-NMR spectra and a broad IR band centered at 1563 cm⁻¹ corresponding to >C=O stretch for disodium salt of succinic acid and
- the peak at $\delta = 6.38$ or 5.91 ppm in ¹H-NMR and the strong band at 1637 cm⁻¹ in FTIR corresponding to -HC=CH- in maleic acid were absent.

Mechanism of electrode reaction

Both maleic and succinic acids are dibasic acids. They dissociate stepwise in two well separated pH regions. Their acid dissociation constants (pK_a and pK_{2a}) corresponding to equilibria 1 and 2 shown below are reported to be 1.75 and 5.82 for maleic acid and 3.92 and 5.12 for succinic acid respectively [10]. These values reveal that the free acid, mono anion and dianion of both maleic and succinic acids exist in equilibrium at pH < 7 but they convert into the dianion at pH > 7.

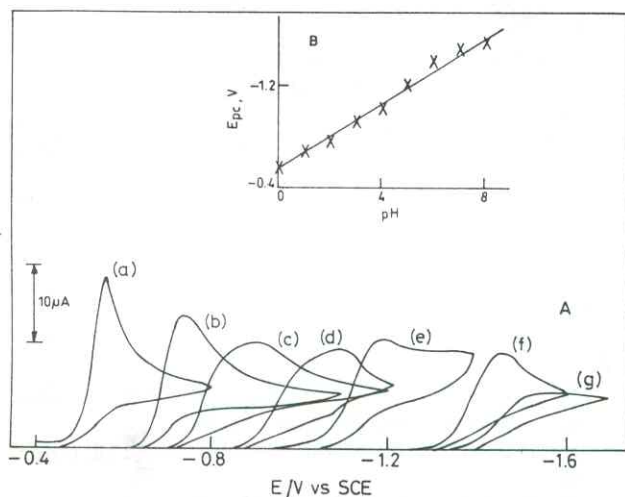
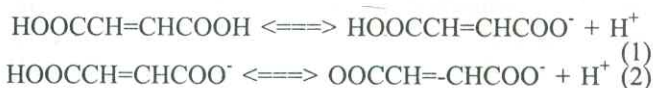


Fig. 2: (A) Cyclic voltammetric response of 1 mM maleic acid at HMDE in buffered and unbuffered media (a) 0 (b) 2 (c) 3 (d) 4 (e) 5 (f) 7 (g) 8.1 Scan rate = 0.1 V/s (B) Plot of E_{pc} vs pH

The split in the plateau of the peak seen in Figs. 2a and d is probably due to the resolution of the reduction steps corresponding to HOOCCH=CHCOOH and HOOCCH=CHCOO⁻ present at equilibrium (Eq. 1).



Then, the reduction peak at less negative potentials may be attributed to the involvement of HOOCCH=CHCOOH while the other at more negative potentials is due to HOOCCH=CHCOO⁻ in the electrode process. This assumption is supported by the observation that a single reduction peak was observed at pH ≥ 5 (Figs. 2A, 2e-g) due to the complete conversion of HOOCCH=CHCOOH to HOOCCH=CHCOO⁻.

Comparison of pK_a values also revealed that one of the carboxylic acids in both maleic and succinic

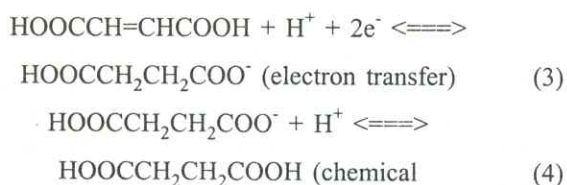
TABLE I: Cyclic voltammetric data of maleic acid reduction at HMDE in buffered and unbuffered media

pH	v (V/s)	i _{pc} (μA)	-E _p (V)	E _{p/2} - E _{p'} (mV)
0.0*	0.05	13.770	0.559	24
	0.10	19.480	0.556	23
	0.50	38.970	0.574	39
1.0	0.05	11.020	0.685	24
	0.10	15.150	0.688	35
	0.50	29.330	0.696	32
2.02	0.05	10.236	0.787	79
	0.10	14.566	0.748	56
	0.50	31.496	0.740	63
3.00	0.05	8.267	0.881	
	0.10	11.417	0.905	***
	0.50	24.409	0.960	
4.10	0.05	8.661	1.078	
	0.10	12.598	1.094	***
	0.50	25.590	1.118	
5.05	0.05	9.055	1.212	70
	0.10	12.204	1.204	70
	0.50	23.622	1.181	70
7.00	0.05	7.874	1.456	55
	0.10	11.023	1.464	55
	0.50	22.047	1.496	87
8.10**	0.05	4.724	1.543	55
	0.10	5.905	1.551	63
	0.50	9.448	1.574	86

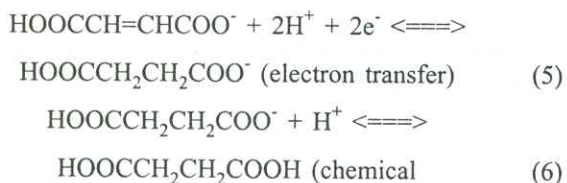
* in 1 M H₂SO₄ ** in 0.1 M Na₂SO₄ *** 2 peaks are observed

acids behaves nearly as a strong acid while the other as a weak acid. However, the more acidic carboxylic group of maleic acid is relatively stronger than that of succinic acid while the second carboxylic acid of maleic acid is relatively weak as compared to that of the succinic acid. Based on these facts and the cyclic voltammetric ($E_{p/2} - E_p$) data given in Table I, the pH dependent nature of the cyclic voltammetric peak at - 0.570 V (Fig. 1a) is explained by the following mechanism of electrode reactions.

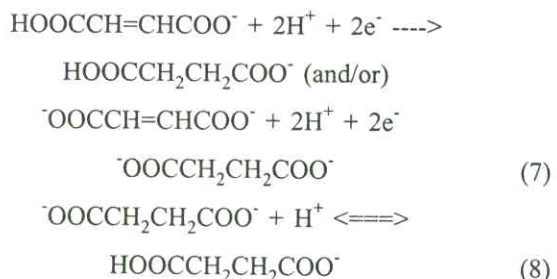
pH 0 to 2.5



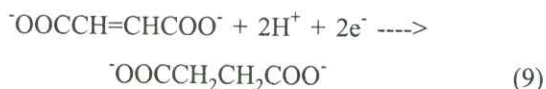
pH 2.5 to 4.5



pH 4.5 to 6.5



pH > 6.5



In 1 M H_2SO_4 or in the pH range 0 to 2.5 maleic acid (HOOCCH=CHCOOH and/or HOOCCH=CHCOO^-) acid is reduced at the electrode by taking 2e^- from the electrode and 2H^+ (one from its more acidic carboxylic acid group and the other from the medium) to give $\text{HOOCCH}_2\text{CH}_2\text{COO}^-$ which rapidly protonates to succinic acid (eqs. 3 and 4). But, in the pH region 2.5 to 4.5 wherein HOOCCH=CHCOOH is converted totally into HOOCCH=CHCOO^- undergoes reduction by taking

2e^- from the electrode and 2H^+ from the medium to give $\text{HOOCCH}_2\text{CH}_2\text{COO}^-$ which again is protonated to $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ (eqns.5 and 6) by abstracting a proton from the solution. In the pH region 4.5 to 6.5 maleic acid is mostly present as a mixture of HOOCCH=CHCOO^- and HOOCCH=CHCOO^- and they undergo $2\text{e}^- \cdot 2\text{H}^+$ change simultaneously at the electrode producing $\text{HOOCCH}_2\text{CH}_2\text{COO}^-$ and $\text{HOOCCH}_2\text{CH}_2\text{COO}^-$, respectively (eq. 5 and 7). The latter product may be in equilibrium with the former one or may rapidly protonate to the former in a succeeding chemical step (eq. 8). On the contrary, at pH > 6.5, where the maleic acid exists solely as HOOCCH=CHCOO^- reduction by $2\text{e}^- \cdot 2\text{H}^+$ occur to give a single product i.e. $\text{HOOCCH}_2\text{CH}_2\text{COO}^-$ (eq. 9).

Electroreduction of MA can occur by (i) the direct electron transfer from the electrode, (ii) the reaction of activated hydrogen ions and/or (iii) the reaction of adsorbed hydrogen ions with it [7].

Due to high hydrogen overpotential in the case of mercury cathodes, reaction (iii) cannot take place and hence, the reduction can occur either by (i) or (ii).

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