

CYCLIC VOLTAMMETRIC STUDY OF SOME MONOACETOXYFLAVONES

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The electrochemical reduction behaviour of six different mono- acetoxyflavones (2', 4', 3-, 5-, 6- and 7-acetoxyflavones) has been studied on glassy carbon electrode (GCE) in Dimethylformamide (DMF) medium with tetrabutylammoniumbromide (TBAB) as supporting electrolyte at different sweep rates. The kinetic parameters such as diffusion coefficient (D) and irreversible charge transfer rate constant for the electrode reaction ($K_{s,h}$) values are evaluated.

Keywords: Monoacetoxyflavones, DMF, GCE, TBAB, cyclic voltammetry

INTRODUCTION

Flavonoid compounds have great significance in biological and pharmaceutical fields. Polarographic studies of certain flavonoid compounds have hitherto been restricted to certain acid/alkaline pH range and attention has been limited to a comparison of reduction potentials [1-4]. It has been clearly established that in a wide range of pH, one polarographic wave of irreversible two electron reduction is obtained. As cyclic voltammetric study of these compounds are expected to provide better understanding of the reduction behaviour, we report here the electrochemical reduction behaviour of six different monoacetoxyflavones (Fig. 1) as a part of our ongoing work [5,6] on these type of flavonoid compounds.

EXPERIMENTAL

The monohydroxyflavones were produced from Bio-organics, Madras and their acetyl derivatives prepared in pyridine with acetic anhydride [7]. They were recrystallied from MeOH/H₂O and tested for their purity. Cyclic voltammetric measurements were carried out with a BAS-100A electrochemical analyser. All chemicals used

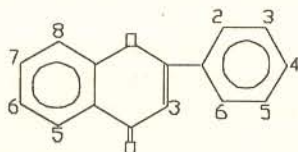


Fig.1 Flavone

were of A.R. Grade and all potentials were measured with reference to a gel type Ag/AgCl electrode (BSA; MF 2020) at $298 \pm 1K$. The glassy carbon disc (5mm dia) was embedded in teflon gasket with provision for electrical connections. It was polished with 1/0 to 4/0 energy papers successively. Platinum wire was used as the counter electrode. Controlled potential electrolysis was carried out and the course of the reaction was followed by UV spectral study.

RESULTS AND DISCUSSION

The monoacetoxyflavones gave a single well defined cathodic wave (Figs. 2 and 3). The cathodic peak current (i_p) increases with increasing sweep rate. The plots of i_p vs $v^{1/2}$ are found to be linear and pass through origin. The current function ($i_p/c v^{1/2}$) has been found to be fairly constant with respect to sweep rates indicating the electrode process as diffusion controlled. The irreversible nature has been seen by the absence of anodic peak in the reverse scan and variation of peak potential with the scan rate.

Controlled potential electrolysis has been carried out and after electrolysis the two electron reduction product was confirmed by its characteristic U.V. absorption maximum value (550 nm) and specific color reactions [8]. The electrode process can be considered as the formation of a monoanion radical [9] by pre- electron addition followed by protonation of the ion-radical. Then the uptake of the second electron occurs with no further requirements of activation energy so that only a single peak is obtained (Scheme 1). The various

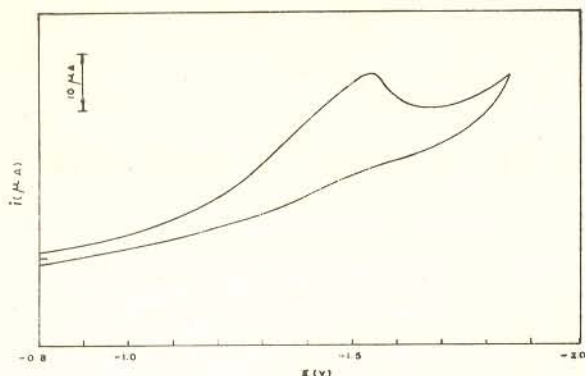


Fig. 2: Typical cyclic voltammogram of compound 4-acetoxyflavone medium - DMF; Sweep rate = 200 mVs⁻¹

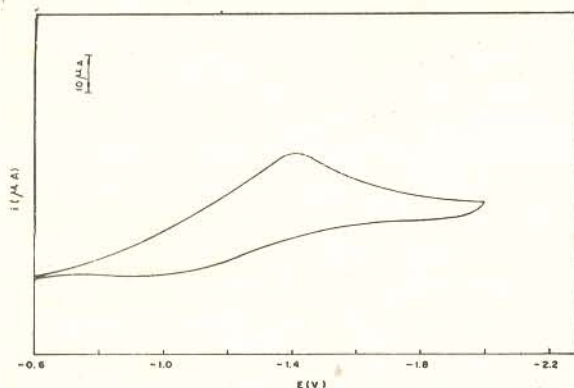


Fig. 3: Typical cyclic voltammogram of compound 7-acetoxyflavone medium - DMF; Sweep rate - 100 mVs⁻¹

kinetic parameters such as diffusion coefficient and the irreversible charge transfer rate constant for the electrode reaction ($k_{s,h}$) are evaluated (Table I) by using the theory of Nicholson and Shain [10]. It has been observed that substitution in a position conjugated to the carbonyl group is capable of affecting the reduction potential of carbonyl group. The decrease in case of reduction is reflected in a shift of the E_p value to more negative side and the lower charge transfer rate constant value.

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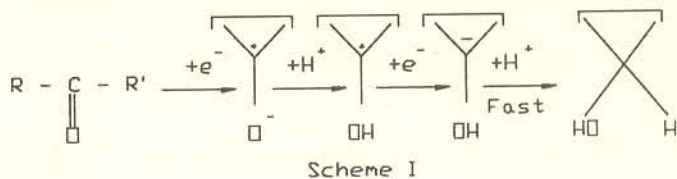


TABLE I: Parameters derived from cyclic voltammetry

Substance (m.pt)	Sweep rate VS ⁻¹	-E _p V	i _p μA	D x 10 ⁶ cm ² s ⁻¹	n	k _{s,h-1} cm s
a	200	1.51	18.38	7.19	0.286	
	100	1.50	12.12	6.37	0.281	7.4023 x
	50	1.45	9.14	7.19	0.283	10 ⁻⁷
	20	1.41	6.09	7.86	0.287	
b	200	1.53	15.12	5.66	0.246	
	100	1.49	12.49	7.81	0.243	
	50	1.47	8.60	7.49	0.241	7.8679 x
c	200	1.43	14.42	5.85	0.216	
	100	1.40	11.22	7.26	0.217	
	50	1.39	7.86	7.05	0.213	9.7942 x
d	200	1.52	12.20	4.19	0.216	
	100	1.46	8.69	4.21	0.218	
	50	1.42	7.22	5.83	0.218	7.8336 x
e	200	1.37	4.68	6.83	0.219	10 ⁻⁷
	200	1.22	18.46	7.59	0.273	
	100	1.15	11.43	5.81	0.274	
f	50	1.09	9.36	7.75	0.275	1.1277 x
	20	1.05	6.04	8.09	0.274	10 ⁻⁶
	200	1.45	14.17	5.25	0.233	
g	100	1.38	10.43	5.71	0.232	
	50	1.37	7.41	5.75	0.232	8.6520 x
	20	1.31	5.20	7.06	0.233	10 ⁻⁷

a = 2'-acetoxyflavone (90) b = 4'-acetoxyflavone (137)
 c = 3-acetoxyflavone (111) d = 5-acetoxyflavone (145)
 e = 6-acetoxyflavone (159) e = 7-acetoxyflavone (130)

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