POLAROGRAPHIC BEHAVIOUR OF 3-ACETYLCOUMARIN

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The polarographic reduction of coumarin [1] in alcoholic medium containing Et_4NBr proceeds in two steps with half-wave potential of -1.66 V and -2.16 V. A single, reversible, 1 electron wave for coumarin was observed in Britton-Robinson buffers [2]. The mechanism of the reduction of coumarin at dme in neutral, aqueous alcoholic solution and in non-aqueous dimethylformamide was investigated [3]. The first wave corresponds to reversible anion-radical formation closely followed by dimer formation and the second wave corresponds to irreversible reduction of the undimerised anion radical. Coumarin [4] undergoes a single one electron reduction to a 4,4'-dimer. Controlled potential electrolysis yields two high melting point lactones, perhaps the meso and dl isomer. Above pH 10, the current decreases, since the lactone ring in coumarin is opened to a non-reducible anion. 4-methoxy-coumarin undergoes two electron reduction to hydrogenate the double bond, whereas 4-hydroxycoumarin [5] enolizes in the other direction and is non-reducible. The present investigation has been carried out to throw light on the polarographic behaviour of 3-acetyl-coumarin in Britton-Robinson buffers.

EXPERIMENTAL

Polarograms were recorded on the DC Pen Recording Polarograph model CL-25, ELICO, India. Saturated Calomel Electrode (SCE) was used as the reference electrode. The pH measurements were made on an ELICO LI-10 pH Meter with glass electrode. The dme had the following characteristics: $m^{2/3}\ t^{1/6} = 2.5\ mg^{2/3}\ sec^{1/2}$.

3-acetylcoumarin, prepared according to the procedure reported [6], was recrystallised from benzene. Stock solution of concentration 50 mM of the compound was prepared in N,N'-dimethylformamide (AR). Britton-Robinson buffers [7] in the pH range 2-10 were prepared in doubly distilled water using AnalaR grade chemicals.

20 ml of the experimental solution, consisting of the depolarizer, appropriate buffer and organic solvent, was taken into a Lingane type H-cell. The solution was deaerated by passing pure nitrogen gas for about 30 minutes, then the dropping mercury electrode was immersed in the solution and the polarograms were recorded at suitable sensitivity in the potential range of study.

RESULTS AND DISCUSSION

3-acetylcoumarin exhibits three waves (i_1, i_2 and i_3) at pH 2 - 4, two waves (i_2 and i_3) at pH 5-8 and a single wave (i_2) at pH > 8 in Britton-Robinson buffer media containing 5% (V/V) of dimethylformamide (Table 1). The half-wave potentials of the three waves were -0.68 V, -0.85 V, and -1.22 V vs SCE respectively and are pH-independent. The limiting diffusion current of wave i_1 decreases with the increase of pH and at pH > 4, it coalesces with the wave i_2. On the other hand, the limiting diffusion current of wave i_2 gradually increases upto pH 8 and then decreases beyond this pH. Wave i_3 decreases steeply after pH 5, disappears completely at pH > 8.

Coumarin is known to give one pH independent wave with $E_{1/2}$ of 1.44 V and currents comparable to that of the third wave of acetyl coumarin and this corresponds to the reduction of the double bond in the lactone ring. At high pH values hydrolysis occurs and the lactone ring opens to give a nonreducible anionic species. This occurs in coumarin at pH > 10 but in acetyl coumarin it occur at pH > 8. The presence of electron with-drawing acetyl group at the third position favours the hydrolysis of the lactone and the current decrease is observed at lower pH values.

The waves i_1 and i_2 of acetyl coumarin corresponds to the reduction of carbonyl group, which is similar to the reduction of chalcone [8], 1-phenyl-2-butenone [9] and 1,5-diphenyl-2,4-penta-dienone [10] and crotonaldehyde [11] At pH > 4, these two waves (i_1 and i_2) coalesces to form a two electron reduction wave. Elving and Leone [12] and Gardner [13] observed the similar behaviour in the polarographic reduction of ketones.

pH-independence of half-wave potentials of all the waves suggest that proton participation in the reduction does not occur before the rate controlling step and suggests that the initial electrode reaction involves the uptake of electron to form a radical anion. Proton participation, if and when it occurs, is a fast

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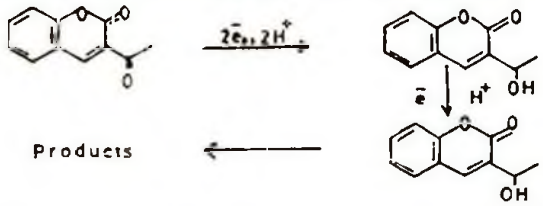
TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF 3-ACETYLCOUMARIN IN BRITTON-ROBINSON BUFFERS 3-ACETYLCOUMARIN + 2.5 mM; DMF + 5% (V/V)

	Acetyl Coumarin						Coumarin				
	I wave			II wave			III wave				
	-E V	i μA	I	-E V	i μA	I	-E V	i μA	I	I
2.0	0.68	4.72	0.755	0.85	7.60	1.22	1.22	10.09	1.61	1.69
3.0	0.68	3.93	0.629	0.80	8.38	1.34	1.22	9.83	1.57	1.57
4.0	0.68	3.54	0.566	0.85	8.78	1.40	1.22	8.12	1.30	1.43
5.0	-	-	-	0.85	9.17	1.47	1.22	7.34	1.17	1.28
6.0	-	-	-	0.85	9.69	1.55	1.22	5.24	0.84	1.15
7.0	-	-	-	0.85	9.83	1.57	1.22	4.45	0.71	1.00
8.0	-	-	-	0.90	10.48	1.67	1.22	2.64	0.42	0.84
9.0	-	-	-	0.90	9.43	1.51	-	-	-	0.71
10.0	-	-	-	0.90	8.38	1.34	-	-	-	0.61

step and does not affect the rate controlling step. The majority of mechanistic studies [14] concentrated on the process involved in the first electron uptake.

The reduction of acetyl coumarin may be represented by the following reaction scheme.



Introduction of an acetyl group at 3-position of coumarin has little effect on the polarographic reduction of ethylenic bond present in the lactone ring of coumarin.

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