Effect of pH on Kinetic Parameters of 6-Substituted Flavones - A Normal Pulse Polarographic Study

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Kinetic parameters of electroreduction of 6-hydroxyflavone and 6-acetoxyflavone in 60% DMF are reported here.

Flavonoid compounds have great significance in biological and pharmaceutical fields. Electrochemical studies of a few flavonoids have revealed an irreversible polarographic reduction wave in a wide range of pH [1]. However, no detailed study of kinetic parameters for the electro reduction of 6-hydroxy and 6-acetoxy flavones in aqueous DMF are reported. So, in continuation of our study of flavonoid compounds [2], we have reported here the kinetic parameters of 6-hydroxy and 6-acetoxy flavones in 60 % DMF of different pH with tetrabutylammonium bromide (TBAB) as supporting electrolyte.

EXPERIMENTAL

6-Hydroxyflavone was purchased from Bio organics, Madras and recrystallised from methanol. Its acetyl derivative was prepared in pyridine with acetic anhydride [3] and characterised (m.p. 158°C) λ_{max} in MeOH 300, 314sh nm, $\nu_{C=O}$ 1750 cm^{-1}. Universal buffers of pH 2 - 12 were prepared using 0.04 M acetic acid, boric acid, phosphoric acid and 0.2 M NaOH. Tetrabutylammonium bromide was the supporting electrolyte. Because of poor aqueous solubility, 60% DMF was used as the solvent. Triton X-100 was used as the maximum suppressor. Test solutions were prepared in solutions of different pH, thermostated (298±1°K) and deaerated before measurement. Owing to the instability of flavonoid solutions in alkaline pH, solid compound was added to cell solution just before measurement.

Normal pulse polarographic model CC-90, coupled with polarocard model CR-108 was used. Glass capillary characteristics: m = 28.88 $mg.sec^{-1}$ and t = 1 sec under open circuit. All potentials were measured against SCE. UV spectra were recorded on JASCO UVIDEC-430B spectrophotometer and pH was measured on Elico pH meter.

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RESULTS AND DISCUSSION

Both 6-hydroxyflavone and 6-acetoxyflavone gave a single, well-defined cathodic wave in all the buffer systems studied over the entire pH range. The limiting current varied linearly with concentration of the flavone and also with the square root of the mercury column height indicating that the waves are diffusion controlled. The electrochemical reduction process was found to be irreversible as evidenced from the variation of reduction potential with concentration of the depolariser, log plot analysis and disobedience of Tome's criteria [4].

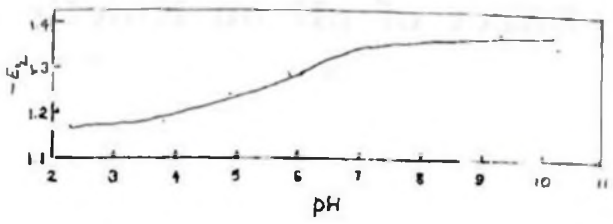


Fig.1 Effect of pH on Halfwave Potential of 6-Hydroxy flavone

Plot of $E_{1/2}$ vs pH shows mainly two segments (Fig 1). This pH dependence is likely to be due to the combined effect of protonation / proton involvement in the rate determining step and direct electron addition. The

Table 1

Polarographic Data

pH	$-E_{1/2}$ V	i_d µA	αn_a	D x 10^6 $cm^2.s^{-1}$	$k^o_{f,h}$ cm. s^{-1}
6-Hydroxyflavone					
2.3	1.166	33.7	0.2612	8.66	1.80 x 10^{-7}
3.8	1.176	32.1	0.2586	7.88	1.72 x 10^{-7}
4.9	1.235	31.9	0.2504	7.83	1.29 x 10^{-7}
5.9	1.271	31.4	0.2452	7.55	1.10 x 10^{-7}
6.8	1.344	29.6	0.2422	6.73	5.67 x 10^{-8}
7.9	1.352	29.1	0.2423	6.48	5.32 x 10^{-8}
8.4	1.360	30.3	0.2492	7.04	3.77 x 10^{-8}
10.2	1.368	30.5	0.2470	7.12	3.90 x 10^{-8}
6-Acetoxyflavone					
2.3	1.140	34.6	0.2701	9.15	1.76 x 10^{-7}
3.8	1.167	35.0	0.2712	9.39	1.29 x 10^{-7}
4.9	1.220	35.0	0.2627	9.37	1.02 x 10^{-7}
5.9	1.246	34.7	0.2625	9.23	7.82 x 10^{-8}
6.8	1.294	33.2	0.2642	8.46	4.28 x 10^{-8}
7.9	1.320	32.2	0.2553	7.95	4.61 x 10^{-8}
8.4	1.326	33.8	0.2514	8.76	5.38 x 10^{-8}
10.2	1.342	33.8	0.2522	8.75	4.44 x 10^{-8}

limiting current decreased with increase in pH in the form of dissociation curve (upto 6.8 in case of 6-hydroxy flavone and upto pH 7.9 in case of 6-acetoxy flavone) and above this it reaches almost a constant value. The half wave potential became slightly more negative with increase in pH. This may be attributed to the decrease in availability of protons with increase in pH.

Controlled potential electrolysis has been carried out and the course of the two electron reduction process was monitored by U.V. - visible absorption peak at 530 nm. The kinetic parameters such as diffusion coefficient (D) and heterogeneous forward rate constant ($k^{o}_{s,h}$) were calculated (Table 1).

CONCLUSION

The reaction rate is fast in acidic medium since protonated form ($C=OH^{+}$) gets reduced. The rate decreased and half wave potential became slightly more negative with increase in pH. αn_a and $k^{o}_{s,h}$ decreased with increase in pH, indicating that the reduction is becoming more and more irreversible with increase in pH. The reduction scheme proposed earlier [2] for keto group appear to hold good here also.

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