Polarographic Study of 2'-Hydroxy-4,4'-dimethoxychalkone at Dropping Mercury Electrode

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2'-Hydroxy-4,4'-dimethoxychalkone undergoes a two-electron polarographic reduction to dihydrochalkone over the pH range, 1·9 to 13·5 (50% ethanolic BR buffers, 0·1N; 0·5N; 1·0N KOH) in two one-electron steps. Limiting current versus pH plot has a minimum at about pH 10·0 due to ring cyclization of chalkone to the corresponding flavanone. Plausible schemes for reduction of the chalkone have been suggested.

CHALKONE exhibits a two-electron reduction at lower pH values and a four-electron reduction in alkaline solutions[1]. Geissman and Friess[2] assumed a two-electron reduction process for a number of chalkones. Tirouflet and Corvaisier[3] examined a number of chalkones from heterocyclic aldehydes and concluded that o-hydroxychalkones undergo cyclization to chromanones at higher pH values. They also calculated[4] the values of equilibrium constant for the chalkone-chromanone equilibria. Dahiya and Bannerjee[5] while investigating the polarographic behaviour of 2'-hydroxy-4',6'-dimethoxy- and 2',4',6'-trimethoxy-chalkones showed that these compounds exhibited two one-electron waves. They also showed that the former compound underwent ring cyclization under mild alkaline conditions. Present study has been conducted to establish the reduction mechanism and to calculate the kinetic parameters of the electro-reduction of 2'-hydroxy-4,4'-dimethoxychalkone.

Materials and Methods

2'-Hydroxy-4,4'-dimethoxychalkone was prepared by the condensation of 2-hydroxy-4-methoxyaceto-phenone with anisaldehyde; m.p. 124°. Other chemicals used were of AR grade. Stock solution (10 ml) was prepared in aldehyde-free absolute ethanol. A typical test solution (10 ml) contained stock solution (1 ml), Britton-Robinson buffer (μ=1·0 with added KCl; 5 ml), gelatin (0·2%, 0·2 mM), made up to the mark with ethanol. The polarographic studies were conducted in the pH range 1·9 to 13·5. The higher pH values were attained by taking appropriate dilutions of KOH, containing KCl, where necessary, to maintain the ionic strength at 0·5.

The test solutions were kept overnight for equilibration, then thermostated in a double-walled Kalousek cell (30°±0·1°C), deaerated by bubbling purified nitrogen for 10 min and polarograms were recorded with pen-recording polarograph, Polariter PO4. The Sargent capillary characteristics were m=1·395 mg sec^{-1} and t=4·8 sec for 80 cm height of mercury column in 0·5 molar KCl at zero applied potential (SCE). The pH values of buffers were measured on a radiometer pH-meter PHM-26 with an accuracy of ±0·01 pH unit.

Effect of pressure-head of mercury on average currents was studied for potentials corresponding to the rising portions of the polarographic waves for two pH values, 5·74 and 12·8 and log $\bar{i}$ versus log h plots were constructed.

The 'n' value was obtained by recording polarograms before and after electrolysis at d.m.e. at constant potential corresponding to the first and second diffusion plateaus.

The number of protons participating in the electrode process was obtained as the ratio of the slopes of $E_{\frac{1}{2}}$ versus pH plot and of semi-log plot.

Kinetic parameters for the first polarographic wave (pH 7·3) were calculated using Koutecky and Cizek's treatments[6,7].

Polarograms were also recorded for different concentrations (0·01-1·0 mM) of the chalkone, pH values 5·3 and 12·8.

Results and Discussion

Typical polarograms of 2'-hydroxy-4,4'-dimethoxy chalkone (1·0 mM; 50% ethanolic, Britton-Robinson buffers and KOH solutions) exhibit two waves. At pH 1·9 only a single wave is observed, the second, presumably having merged with that of supporting electrolyte. A single wave is also seen for pH 7·88. For all other pH values two well-separated waves are observed, the height of the second wave being consistently slightly smaller than that of the first.

Plots of the limiting currents of waves and of the total limiting currents against pH exhibit inverted parabolic characters, with a minimum at about pH 10·0 (Fig. 1). A new more negative wave comprising of the balance of the limiting current is also seen on keeping the solution for a week. A slight fall in total current is observed for solutions in potassium hydroxide.

TLC examination (on silica gel G) of the test solutions (pH values 4·75 and 13·5) exhibited single spots which matched with that of chalkone (R$_f$ 0·88;

TABLE 1 — E-1/2 pH SLOPES; WAVE SLOPES AND TRANSFER COEFFICIENTS CORRESPONDING TO EACH WAVE AT DIFFERENT pH VALUES

pH	2·89	3·78	4·78	5·74	6·3	6·9	7·3	7·88	9·36	10·38	11·4	12·8
(Slope)₁	0·056	0·063	0·08	0·09	0·087	0·08	0·071	0·065	0·056	0·06	0·06	0·067
α_1	←—— 1·0 ——→			←——— 0·74 ———→				←——————— 1·0 ———————→				
(Slope)₂	0·087	0·079	0·08	0·06	0·067	0·60	0·078		0·075	0·075	0·07	0·074
α_2	←——— 0·73 ———→			←——— 1·0 ———→				←——————— 0·84 ———————→				
pH	Up to 3·2		Between 3·2 and 7·1				Between 7·1 and 11·2			Above 11·2		
E½-pH (Slope)₁ (V)	0·11		0·054				0·0			0·077		
pH	Up to 5·8		Between 5·8 and 7·5				Above 7·5					
E½-pH (Slope)₂ (V)	0·014		0·10				0·0066					

Fig. 1 — Plots of current versus pH (chalkone concentration 1·005 mM)
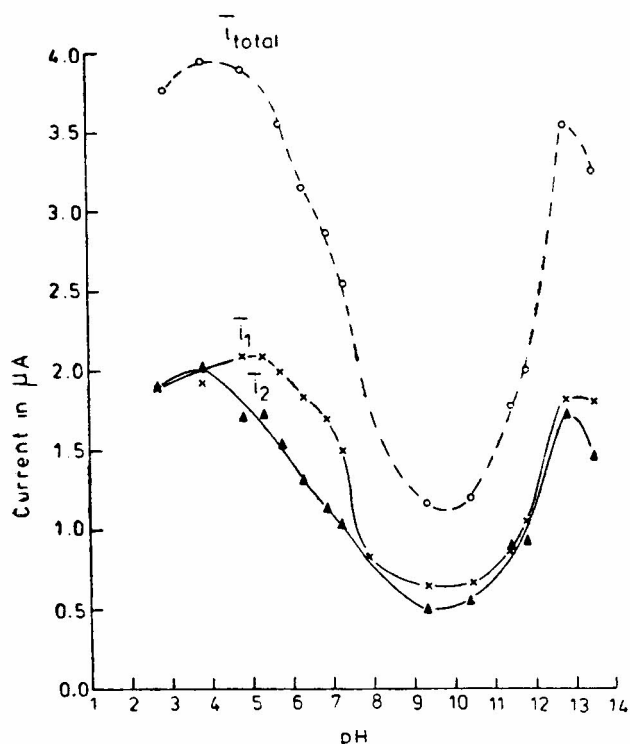

[Fig. 2 — Plots of half-wave potential versus pH (chalkone concentration, 1·005 mM)

irrigating medium, 5% ethyl acetate in b.nzene). The solution at pH 9·91 gave also a second spot (R$_f$ 0·71) which matched with that of isomeric flavanone. These results confirm formation of flavanone from chalkone in mild alkali.

The $E_½$ versus pH plot for the first wave (Fig. 2) consists of four linear segments (a), (b), (c) and (d), having slopes 0·11, 0·054, 0·0 and 0·077 V pH⁻¹ unit and intersecting at pH values 3·2, 7·1 and 11·2 respectively. The plots for the second wave (Fig. 2) has three linear portions (e), (f) and (g) with slopes 0·014, 0·10 and 0·0066 V pH⁻¹ unit, intersecting respectively at pH values 5·8 and 7·5. In Table 1 are given the $E_½$-pH slopes, wave slopes and transfer coefficients corresponding to each wave for different pH values.

The exponent of mercury pressure shows that the average currents corresponding to the rising portions of the polarographic waves range from
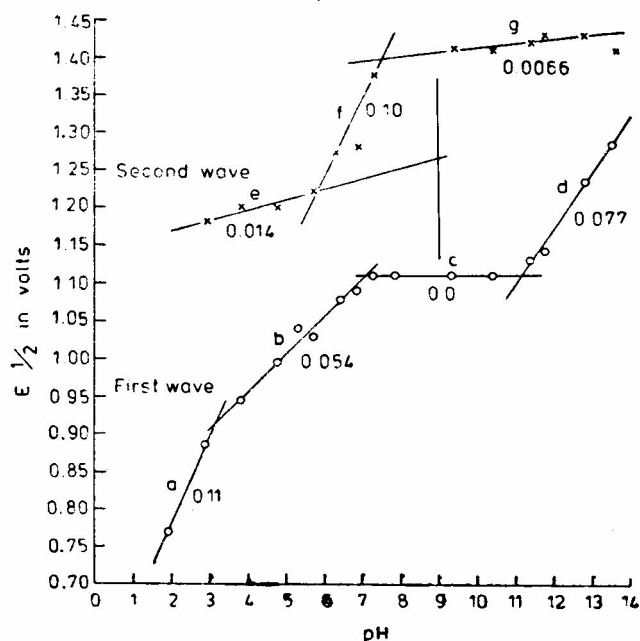
0·0 to 0·46 at pH 5·74; at pH 12·8 it is nearly constant (0·56) for the first wave and varies between 0·38 and 0·65 for the second wave. The waves are, therefore, irreversible for acidic solutions. For alkaline solutions the first wave is diffusion-controlled while the second one is irreversible.

Total limiting current showed a linear dependence on concentration, diffusion current constants having values 0·242 (pH 5·3) and 0·217 (pH 12·8). The increase in [chalkone] at constant pH and ionic strength, does not affect the half-wave potentials significantly.

Millicoulometric results[8] for the total limiting current (pH 4·35) and for the first polarographic wave (pH 9·72), given in Table 2, show that two electrons are consumed per molecule, one electron over each wave. The final product should be, on analogy[1], a dihydrochalkone. A TLC comparison with Pd-C reduction product proved its identity (R$_f$=0·53; irrigating medium 5% ethyl acetate in benzene).

Heterogeneous rate constants over the first polarographic wave (pH 7·3) at the reference poten-

TABLE 2 — MILLICOULOMETRIC RESULTS FOR THE TOTAL LIMITING CURRENTS AND FOR THE FIRST POLAROGRAPHIC WAVE

First wave $(i_c)_1$, (μA)		Total wave (i_c) (μA)		n value	
Before electro-lysis	After elect. (t sec)	Before elect.	After elect. (t. sec)	First wave	Total wave

pH 4·35; [CHALKONE] = 0·1 mM; vol. 1·0 ml

—	—	0·561	0·496 (3600)	—	1·7
			0·480 (6000)	—	2·24
			0·416 (9600)	—	1·88

pH 9·72; [CHALKONE] = 1·0 mM; vol. 1·0 ml

0·442	0·382 (3600)	—	—	1·25	—
	0·333 (7200)	—	—	1·07	—
	0·300 (10800)	—	—	1·24	—

TABLE 3 — HETEROGENEOUS RATE CONSTANTS OVER THE FIRST POLAROGRAPHIC WAVE
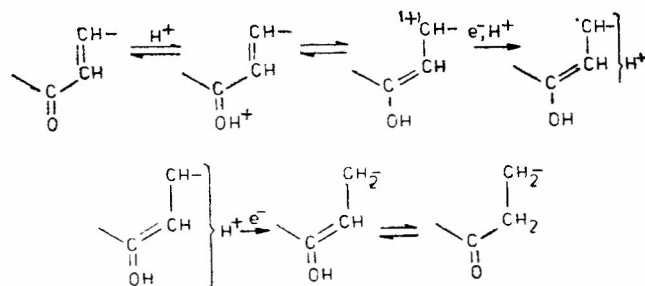
[$D = 0·04266$ cm²/sec; $\xi = 0·11332$]

Potential (V)	i/i_d	χ_1	t (sec)	$\log k_f$	
1·06	0·11	0·2	4·53	$\overline{4}·1163$	(4·429)
1·1	0·35	0·9	4·50	$\overline{4}·6111$	(3·812)
1·12	0·49	1·6	4·48	$\overline{3}·0217$	(5·147)
1·16	0·73	4·5	4·44	$\overline{3}·4729$	(4·007)

$\log k_f$ (versus NHE) $\times 10^{16}$ are given in parentheses.
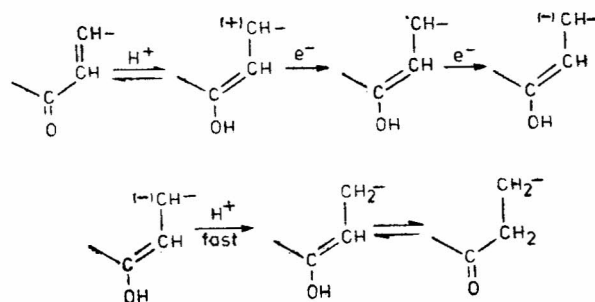

SCHEME 1

SCHEME 2

SCHEME 3(a & b)

SCHEME 4

tial of normal hydrogen electrode have been calculated (Table 3).

Course of electrode process — $E_{\frac{1}{2}}$ versus pH slopes of processes involving irreversible electroreduction with simultaneous or prior protonation[9] are equal to $2·3\ pRT/\alpha nF$, where p is the number of protons involved per molecule of the reducible species. Since the reciprocal slopes of the semilog plots are equal to $2·3RT/\alpha nF$, the number of protons, p is obtained as the quotient of these two parameters. The knowledge of number of protons involved over each of the two one-electron steps can then be used to suggest the scheme of reduction over each of the linear portions of the $E_{\frac{1}{2}}$ versus pH plot. Thus five different schemes (1-5) of reduction are suggested.
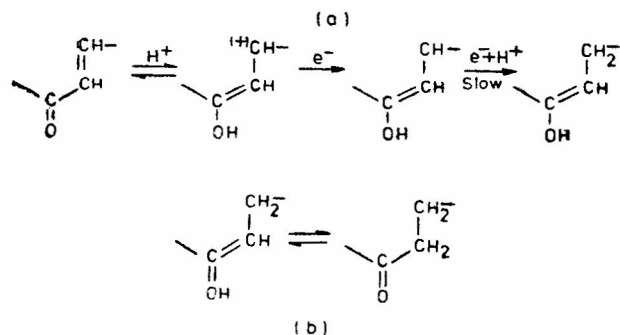
Up to pH 3·2, two-proton dependence of the first wave and proton-independence of the second wave can be explained on the basis of Scheme 1. Between pH 3·2 and 5·8, only the first wave is proton-dependent. The process is, therefore, governed by a prior protonation followed by two successive electron-transfers (Scheme 2). Between pH 5·8 and 7·1,
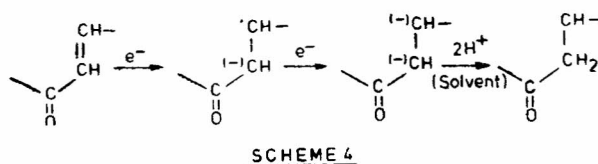
a protonation step prior to first electron-transfer appears to occur side by side with a proton-independent first step (since $p < 1·0$). The second electronation step appears also to involve both one and two protons ($1·0 < p < 2·0$) (Schemes 3a and b). Between pH 7·1 and 11·2 both the polarographic one-electron waves are pH-independent and protons are supplied to the bi-anion by the solvent (Scheme 4). Above pH 11·2 one proton-depen-
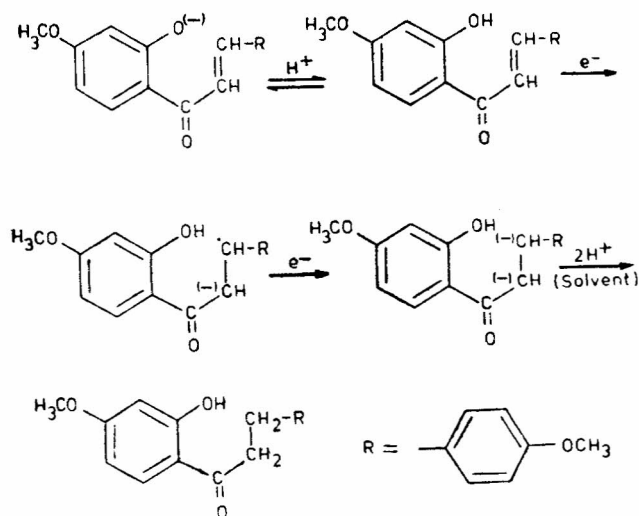
SCHEME 5

dence of the first step and proton-independence of the second step indicates that the chalkone is reduced in o-hydroxy form rather than as phenolate ion as shown in Scheme 5.

References

1. Ryvolova-Kejharova, A & Zuman, P., *J. electroanal Chem.*, **21** (1969), 197.
2. Geissman, T. A. & Friess, S. L., *J. Am. chem. Soc.*, **71** (1949), 3893.
3. Tirouflet, J. & Corvaisier, A., *Bull. Soc. chim. Fr.*, (1962), 535.
4. Tirouflet, J. & Corvaisier, A., *Bull. Soc. chim. Fr.*, (1962), 540.
5. Dahiya, H. P. & Bannerjee, N. R., *Indian J. Chem.*, **14A** (1976), 754.
6. Koutečky, J., *Colln Czech. chem. Commun.*, **18** (1953), 597.
7. Koutečky, J. & Cizek, J., *Colln Czech. chem. Commun.*, **21** (1956), 836.
8. Lingane, J. J., *J. Am. chem. Soc.*, **67** (1945), 1916.
9. Heyrovsky, J. & Kuta, J., *Principles of polarography* (Czechoslovak Academy of Sciences, Prague), 1965, 257.