

Polarograms of 2'-Hydroxy-4',6'-dimethoxychalkone in Aqueous Ethanolic BR Buffers

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Unlike the four-electron polarographic reduction of unsubstituted chalkone, 2'-hydroxy-4',6'-dimethoxychalkone undergoes a two-electron polarographic reduction over the pH range 1.8 to 13.9 (50% ethanolic BR buffers, 0.1N, 0.5N and 1.0N KOH). The process comprises two one-electron steps in acid and alkaline solutions, while it occurs in a single step at intermediate pH values. Above pH 6.0, the limiting current decreases, goes through a minimum at pH 10.9 and increases again to its original value in 0.1N KOH solution. The formation of flavanone in the pH range 9.2 to 12.0 has been indicated by TLC. After analysis of data, namely $E_{1/2}$ versus pH plots, $\log i$ vs $\log h$ plots, commutated (Kalousek) and normal polarograms, and effects of concentration on polarograms, suitable schemes have been suggested for reduction at different acidities.

GEISSMAN and Friess¹ examined the polarograms of a number of chalkones at four pH values and put forward a tentative two-electron mechanism for their reduction. Tirouflet and Corvaisier² concluded that *o*-hydroxychalkones underwent cyclization to chromanones as the pH was increased. They suggested a scheme for the reduction of chalkones and calculated³ the values of equilibrium constants for chalkone-chromanone equilibria. Ryvolova-Kejharova and Zuman⁴, on a detailed examination of polarographic behaviour of unsubstituted chalkone, concluded that it is reduced up to dihydrochalkone by a single two-electron step and at higher pH values up to secondary alcohol by another two-electron step. Four one-electron steps were found at intermediate pH values. An organomercury compound was also formed as a side product in the first electron step. Detailed mechanism for reduction of unsubstituted chalkone was worked out by these authors. Present study has been conducted to establish the mechanism for electrochemical reduction of 2'-hydroxy-4',6'-dimethoxychalkone and to examine the effect of 2'-hydroxyl group on the reduction of -COCH=CH moiety.

Materials and Methods

2'-Hydroxy-4',6'-dimethoxychalkone was prepared by the condensation of phloroacetophenone 4,6-dimethyl ether with benzaldehyde and crystallized from ethanol (m.p. 91-92°). The other chemicals were of AR grade. A stock solution of the chalkone ($1 \times 10^{-2}M$) was prepared in ethanol. A typical 10 ml of test solution contained 0.2 ml of stock solution, 4.9 ml of BR buffer ($\mu = 1.0$ with added KCl), 0.1 ml of 0.5% gelatin and 4.8 ml of ethanol. Test solution was thus $2 \times 10^{-4}M$ in depolarizer, 0.005% in gelatin, 50% with respect to ethanol and had ionic strength of 0.5. Study was conducted in the pH range 1.8-13.9 (BR buffers at 20°, 0.01, 0.1, 0.5N and 1N KOH at 30°C).

The test solutions in double-walled Kalousek cell were kept for 20 min for equilibration ($20^\circ \pm 0.1^\circ$), deaerated by bubbling nitrogen for 10 min and the polarograms recorded using a pen-recording polarograph, Polariter PO4. The Sargent capillary had the characteristics, $m = 1.973 \text{ mg sec}^{-1}$ and $t = 3.5 \text{ sec}$ for 80 cm height of mercury reservoir in 0.5M KCl solution at zero applied potential with respect to SCE. pH values of buffers were measured on a Radiometer pH-meter PHM-26 with an accuracy of ± 0.1 pH unit.

Reversibility of the polarograms was tested at various pH values by recording commutated polarograms using Kalousek commutator switch in conjunction with Polariter PO4.

Polarograms were also recorded at different heights (h) of mercury reservoir for three pH values 3.3, 6.1 and 10.5. Average currents for a series of potentials were read out over these polarograms and plots of $\log i$ versus $\log h$ were constructed⁵. The slopes of these plots also gave indication about their reversibility.

The height of the individual polarographic waves were read from the polarograms. The number of electrons, n , involved in the reduction was evaluated by comparing polarogram of unsubstituted chalkone with that of the hydroxychalkone. The number of protons, p , participating in the electrode process was obtained from the ratio of the slopes of $E_{1/2}$ versus pH plots and of the semi-log plots of the individual waves.

Kinetic parameters for the first polarographic wave of the hydroxychalkone were calculated using Koutecky *et al.*'s treatments^{6,7} using the following relations:

$$i/i_a = \bar{F}(\chi_1) - \xi \bar{H}(\chi_1)$$

where $\chi_1 = k_f \sqrt{12t/7D}$ and $\xi = 50.4D^{1/2}m^{1/3}t^{1/6}$, $\bar{F}(\infty_1)$ and $\bar{H}(\chi_1)$ are tabulated functions, and $\log k = \log k_{\text{NHE}} - \alpha n F / 2.3RT(E - E_{\text{NHE}})$

where k_{NHE} is the rate constant at the potential of normal hydrogen electrode. αn value was obtained from the slope of semi-log plot and D was obtained by applying Ilkovic equation to the total current.

Polarograms were also recorded for concentrations (0.3, 0.6, 0.9, 1.2 and 1.5 mM) of the chalkone at pH values 3.3, 6.6 and 10.4 in order to determine the effect of concentration on the nature of the polarographic waves.

Polarograms of the chalkone (0.2 mM) were also recorded at varying ionic strengths of the media (0.05, 0.1, 0.5 and 1.0) at pH values 3.1, 6.2 and 10.1 to examine the effect of ionic strength on the electrode process.

Results and Discussion

The polarograms of 2'-hydroxy-4',6'-dimethoxychalkone (0.2 mM; 50% ethanolic BR buffers) for various pH values show that up to pH 4.8 these consist of two nearly equal waves (Fig. 1). The second wave is, however, not well defined at pH 1.8. The two waves merge into a composite wave between pH 5.3 and 7.2, but the latter splits into two waves at pH \geq 7.5. The slopes of the waves at different pH values are given in Table 1.

Plots of the limiting currents of the waves against pH show that total current remains almost constant up to pH 6.0 and then decreases with increasing pH from 1.04 μamp (pH = 6.0) to 0.27 μamp (pH = 10.8) in the form of a dissociation curve with inflexion point at pH 9.2. The limiting current again increases asymptotically for pH \geq 10.9 and attains an identical value in 0.1N KOH as it had in acidic media. The inflexion point is at pH 11.9.

TLC of the chalkone kept for 30 min in buffer of pH 9.5 exhibits an additional spot which has been identified as that for the corresponding flavanone. This fact explains the diminution of polarographic current, as the flavanone wave is not observable at the d.m.e. under the conditions of experiment. Increase in current at higher pH values is due to reversal of the process, flavanone being less stable at higher alkalinity. The proposed mechanism is given in Scheme 1.

TABLE 1—THE SLOPES OF THE WAVES AT VARIOUS pH VALUES

pH	Slope of the waves in mV	
	(i)	(ii)
1.9	50	—
3.3	50	75
4.8	50	65
6.1	50	50
8.4	52	68
9.2	50	60
10.0	53	57
10.9	52	58
11.4	45	55
11.8	47	55
0.1N KOH	47	50
0.5N KOH	30	35
1.0N KOH	20	35

Comparison of the polarograms of the *o*-hydroxychalkone with that of unsubstituted chalkone shows that the reduction involves two electrons and hence the process goes up to the dihydrochalkone stage in the pH range 1.8-13.9. This may be due to the dihydrochalkone getting reduced at more negative potentials than that for the reduction of the supporting electrolyte.

The $E_{\frac{1}{2}}$ versus pH plots for the two waves have been depicted in Fig. 2. The $E_{\frac{1}{2}}$ values for composite waves (pH 5.3-7.2) have been obtained as follows: Semi-log plot of such a polarogram (pH 6.1) shows a break at -1.1 V (Fig. 3a). Semi-log plots for the two parts (Figs. 3b and 3c), each assumed to be due to a different process, have been again constructed and the two $E_{\frac{1}{2}}$ values have been read out. The $E_{\frac{1}{2}}$ -pH plot for the first wave consists of five linear portions (a), (b), (c), (d) and (e), having slopes of 72 mV, 50 mV, 10 mV, 68 mV and 16 mV pH^{-1} respectively and intersecting at pH values 3.4, 7.6 and 10.5. $E_{\frac{1}{2}}$ values of the second wave fall on another curve having four linear and one curved portions (f), (g), (h), (i) and (j) with slopes 34 mV, 12 mV, 100 mV, 8 mV and 16 mV pH^{-1} respectively, intersecting at pH values 2.6, 6.6, 8.5

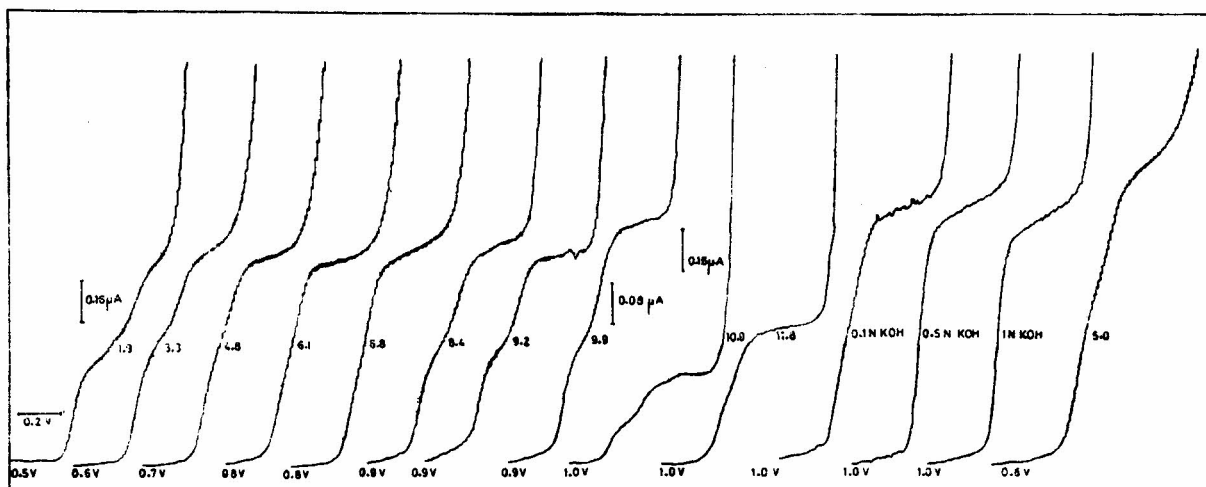


Fig. 1—pH dependence of waves of 2'-hydroxy-4',6'-dimethoxychalkone (0.2 mM), pH's and starting voltages (vs SCE) are indicated in the polarograms

and 10.8. Unusual increase in $E_{1/2}$ in 0.1N KOH for the second wave is being left unexplained.

Normal and commutated polarograms (Fig. 4) show that up to pH 7.6, there are no anodic waves, between pH 7.6 and 11.8 there are small anodic currents, but in 0.5N KOH the compound yields no anodic waves for the first and the second waves have been depicted in Fig. 5. The plot for

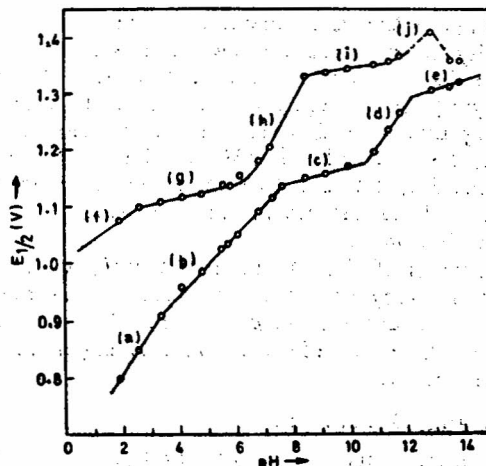
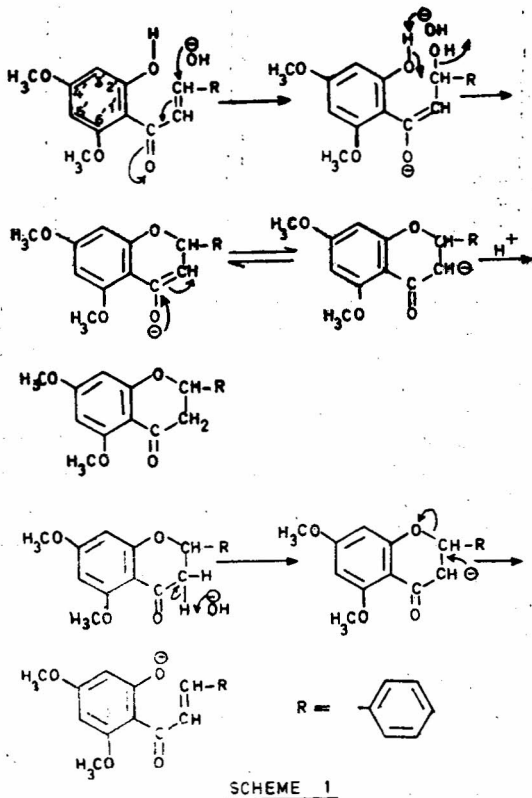


Fig. 2 — pH dependence of half wave potentials: (i) curve abcde, first wave; (ii) curve fghij; second wave

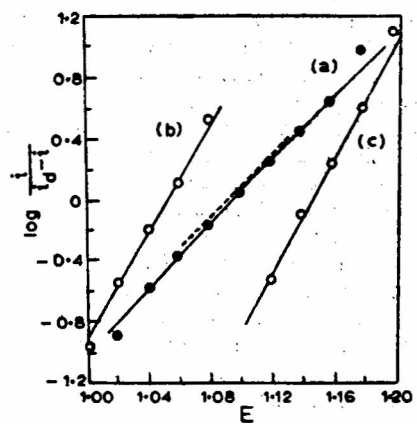


Fig. 3 — Semi-log plots of composite polarogram (pH 6.1)

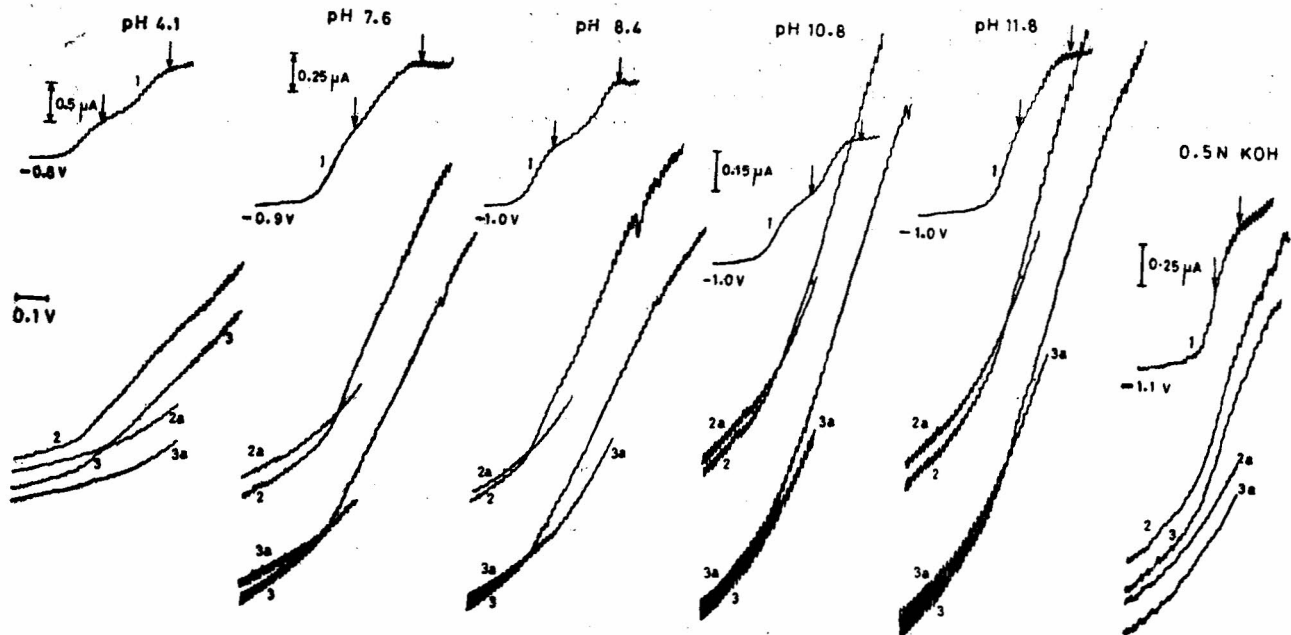
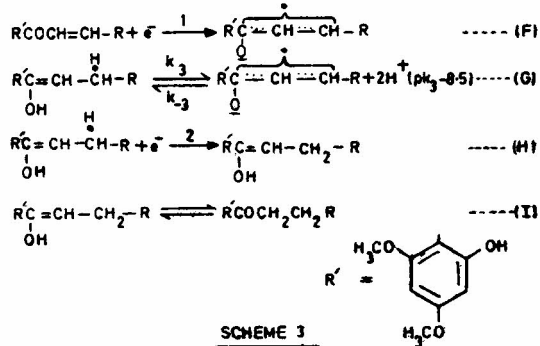
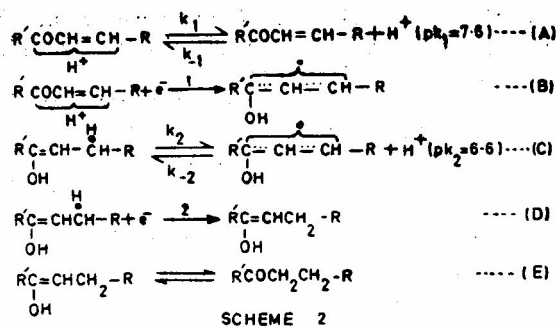


Fig. 4 — pH dependence of the waves of the product (commutator technique) [0.2 mM of the compound, BR buffers; frequency 6 Hz, pH values, starting voltages and auxiliary potentials are given in the polarograms; (1) normal polarogram, (2) and (3) commutated wave with the compd, and (2a) and (3a) residual current with commutator]



the first wave goes through a minimum at pH 9.4 and a maximum at pH 10.9. These correspond to the portions (c) and (d) respectively of the E_1 - pH plot (Fig. 2) and corresponds to the steps F and G of the proposed Scheme 3. The protonation of the mesomeric radical intermediate in Scheme 2 decreases the reversibility of the first step; at higher pH values (10.9) the concentration of the unprotonated radical ion intermediate is considerable and hence the anodic wave comprises appreciable current. i_a/i_d plot for the second wave passes through a minimum between pH 9.0 and 10.8 indicating that the step (H) is almost irreversible. Beyond pH 10.9 (step M) stability of the dianion appears to be appreciable. This also explains the increase in anodic current corresponding to the second polarographic step.

The effect of pressure head of mercury on mean currents has been studied at three pH values, viz. 3.3, 6.1, 10.9. At pH 3.3, the slopes of the $\log i$ - $\log h$ plots (Fig. 6a) for the first wave vary from 0.25 at the foot to 0.4 at the limiting current plateau, thereby indicating the kinetic-controlled nature of the wave. In the case of second wave (Fig. 6b) the slopes vary from 0.3 to 0.5, indicating the kinetic-controlled nature at the early parts of the wave. At pH 6.1, the slopes of the $\log i$ - $\log h$ plots (Fig. 6c) range from 0.4 at the early parts of the wave to 0.5 at the limiting current plateau, showing that the wave is largely diffusion-controlled. For the second wave (Fig. 6d), the slopes are constant and equal to 0.3 indicating the kinetic-controlled nature of the wave. At pH 10.9, the slopes of the $\log i$ - $\log h$ plots (Fig. 6e) vary from 0.20 at the foot to 0.45 at the limiting current plateau of the first wave while these slopes are constant (0.55) for the second wave (Fig. 6f). The early part of the first wave, thus, appears to be controlled by the rate of electrode processes, while the second wave is diffusion-controlled.

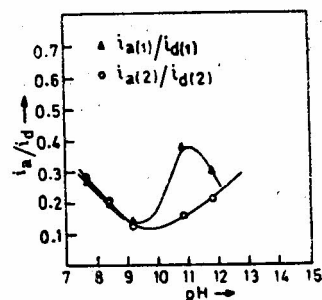


Fig. 5 — pH dependence of ratios of anodic limiting current to the cathodic limiting currents of waves (1) and (2)

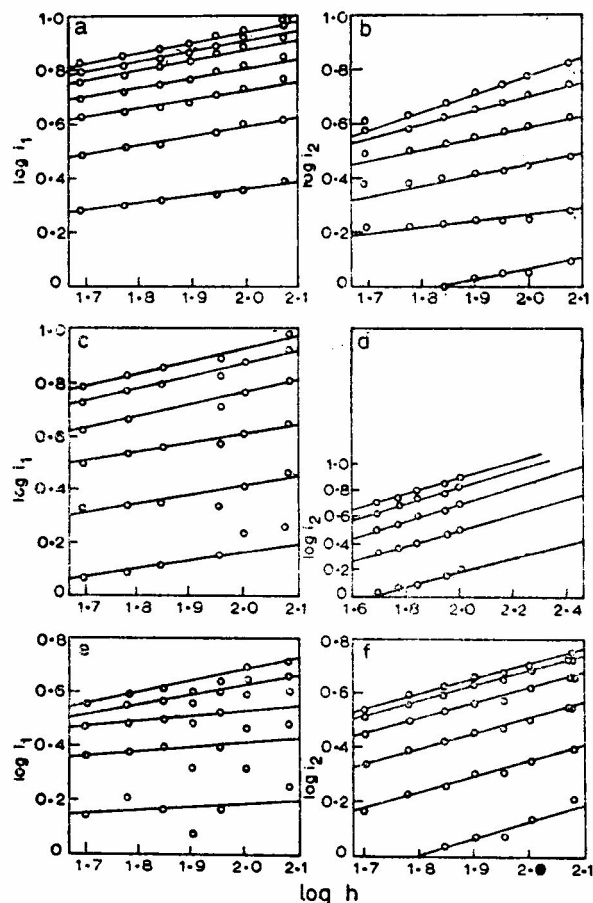
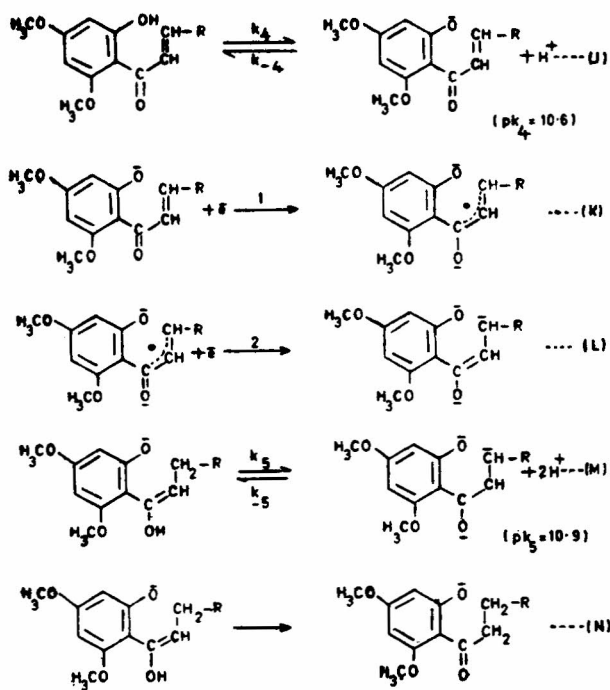


Fig. 6 — \log - \log plots of mean current against mercury head (h) [Applied potential ($-V$) (reading from lowest lines) pH 3.3, (a) first wave: 0.90, 0.92, 0.94, 0.96, 0.98, 1.00, 1.02; (b) second wave: 1.08, 1.10, 1.12, 1.14, 1.16, 1.18; pH 6.1; (c) first wave: 1.00, 1.02, 1.04, 1.06, 1.08, 1.10; (d) second wave: 1.12, 1.14, 1.16, 1.18, 1.20; pH 10.9; (e) first wave: 1.18, 1.20, 1.22, 1.24, 1.26; (f) second wave: 1.32, 1.34, 1.36, 1.38, 1.40, 1.42]

Limiting current of each wave was found to be a linear function of concentration and E_1 values were independent of it. Diffusion current constants were 1.846 and 1.895 at pH 3.3 and 6.6 respectively.

Kinetic parameters of the first polarographic step of the chalkone (0.25 mM, pH 5.0) indicate that the process is in the border line of reversibility. The data used are D , 1.44×10^{-5} $\text{cm}^2 \text{sec}^{-1}$, $\alpha n = 1.7326$, $\xi = 1.879 \times 10^{-1}$. For $i/i_d = \bar{F}(x_1)$ $-\bar{\xi} \bar{H}(x_1) = 0.5$, x_1 has been found to be 1.7 and



SCHEME 4

E vs NHE = -0.785 V. Drop time, t at this potential is 3.32 sec. The values of k_f and k_{NHE} are $2.7 \cdot 10^{-8}$ and $2.16 \cdot 10^{-8}$ respectively.

Up to pH 7.6 each of the steps requires pre-protonation and a tentative mechanism is given in Scheme 3. Between pH 7.6 and 10.5, the second step is dependent on two protons and Scheme 2 should be operative in this region of pH values. Between pH 10.5 and 12.2, ionization of the hydroxyl group appears to precede reduction and Scheme 4 would take care of this equilibrium. Above pH 12.2, ionization of 2'-hydroxyl group does not appear to control the reduction process and steps K, L, H and N in Scheme 4 would be operative in this pH region.

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