Kinetics of Electrochemical Reduction of Benzaldehyde, p-Chloro- & p-Methyl-benzaldehydes in Acidic Solutions

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Kinetics of electrochemical reduction of benzaldehyde, p-chlorobenzaldehyde and p-methylbenzaldehyde have been studied in aqueous acidic solutions at a mercury pool electrode using controlled potential electrolysis and potentiostatic steady-state techniques. The effect of acidity change on the reaction has been studied by applying Bunnet's treatment. Electrochemical reaction orders and ionic exchange current densities have been evaluated. A reduction mechanism is suggested on the basis of the experimental results.

POLAROGRAPHY, associated with preparative electrolysis and coulometry[1-4], a.c. polarography[5], linear sweep voltammetry[16-17] and rotating -ring disc electrode technique[18,22] have been widely employed for the study of mechanism of reduction of aromatic carbonyl compounds. Polarographic studies, in general, have shown that the electrochemical reduction of carbonyl compounds in acid solutions, involves two one-electron steps. In the case of benzaldehyde pinacol is found to be the predominant product at the potential of the limiting current of the first one-electron wave which is stated to correspond to the reduction of the protonated form[14]. The dimerisation is irreversible and rate-determining[23]. The dimerisation has been shown to be one of a rate-determining coupling between a neutral ketyl radical and ketyl radicalanion preceded by a fast and equilibrated protonation eventually followed by neutralisation of the pinacolate,[16,23,24]. Controlled potential coulometric study by Puglise and others[11] also showed that benzaldehyde undergoes reduction on mercury electrode to form hydrobenzoin in acid media. Puglise et al.[11] were interested in the stereochemical aspects of the electrolytic reductive coupling of benzaldehyde.

The present study attempts to investigate the mechanisms of the electrochemicalre ductions of benzaldehyde p-methylbenzaldehyde and p-chlorobenzaldehyde by correlating the rate constants evaluated by controlled potential measurements with the acidity function values. According to Zucker[25] and Hammett[26] the logarithm of the rate constant k varies linearly with acidity function H_o, with a unit slope when the rate-determining step in the conversion of the protonated substrate SH^+ to the transition state does not involve interaction with water. When $\log k$ varies linearly with $\log C_{H^+}$ with a unit slope, the rate-determining step becomes bimolecular with the involvement of water. The exact requirements of Zucker-Hammett hypothesis are rarely obeyed. Bunnett[27] and others[29] studied a large number of hydrolytic reactions and showed that the plots of $\log H_o$ versus $\log a_{H_2O}$ and $\log k + H_o$ versus $H_o + \log C_{H^+}$ were linear

with slopes ω and ϕ respectively which inturn are suggestive of different reaction mechanisms.

Materials and Methods

Benzaldehyde was distilled under reduced pressure and stored under nitrogen atmosphere. The aldehyde solutions were prepared in absolute ethyl alcohol such that 1 ml of stock solution contained the required strength. The p-methyl- and p-chloro-benzaldehydes used were Riedel samples.

Analar samples of hydrochloric acid, sulphuric acid and 70% perchloric acid were employed for the preparation of the solutions of supporting electrolytes of different molarities.

The standard type of circuit for controlled potential coulometry described by Lingane[29] was used. The potential of the cathode was controlled by a set of rheostats. The direct current was supplied by a selenium rectifier. Saturated calomel electrode was used as the reference electrode. The auxiliary electrode was a spiral platinum wire. An efficient magnetically stirred mercury pool served as the working electrode. The rate of stirring was kept constant by a voltage stabilizer. Reduction was carried out in an H-shaped cell given by Lingane wherein the catholyte and anolyte were separated by a sintered glass diaphragm of porosity 4.

Acid (50 ml) of desired strength was taken in the working electrode compartment. The auxiliary electrode compartment was also filled by the same acid until the levels of the acid in both the compartments were equal. The solution in the working electrode compartment was deaerated by bubbling purified nitrogen for 15 min, and mercury (20 ml) added to the working electrode compartment. The acid level in the other limb was adjusted to equal the level in the cathode compartment. The pre-electrolysis was carried out for 15 min with the cathode potential fixed at a value which was to be used for the subsequent reduction of aldehydes. When the background current reached a constant value, an aliquot of known concentration of the aldehyde solution was added to the catholyte and the electrolysis started at the controlled cathode potential. The
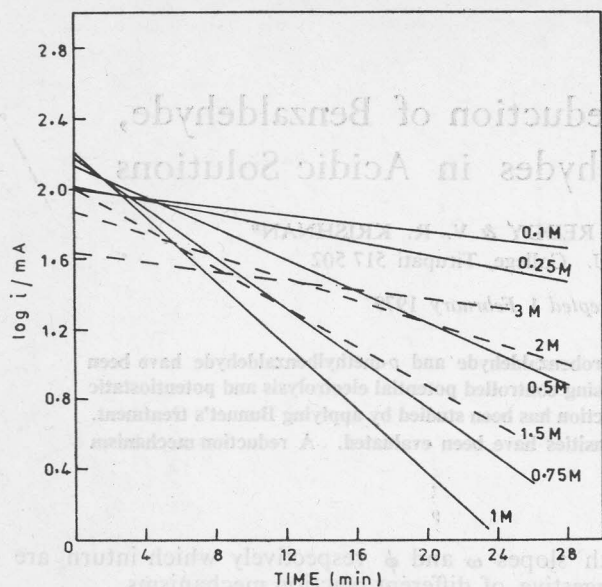
Fig. 1 — Log i versus time plots for benzaldehyde in HCl.

Fig. 2 — Log i versus η plots of benzaldehyde in HCl.

potentials employed for benzaldehyde, p-chlorobenzaldehyde and p-methylbenzaldehyde were respectively –1.04, –1.05 and –1.00 V versus S C E. Nitrogen was bubbled through the catholyte throughout the experiment. The current gradually decreased in the course of experiment. The current readings were noted by sensitive milliammeters in the circuit. at different time intervals. The plots of logrithm of the current vs time plots were linear (Fig 1). These plots have been used to calculate the rate constants. The same procedure was repeated at different concentrations of acid ranging 0.1 M to 3 M. The rate constants were measured in three mineral acids, HCl, H_2SO_4 and $HClO_4$.

The kinetic parameters of the reduction have been evaluated by potentiostatic steady-state technique, the theoretical principles and experimental details of which have been given elsewhere[30].

Results and Discussion

The number of electrons involved in the electrochemical reduction of three aldehydes used was found to be one. This is in agreement with the observations of previous workers [11,31-33].

The rate constants and ionic exchange current density values for benzaldehyde, p-chlorobenzaldehyde and p-methyl benzaldehyde at different concentrations of the acids employed are given in Table 1. For all the aldehydes, the rate constants increase only till one molar acid concentration beyond which the rate constants decreased. However, the exchange current density values presented in Table 1 show that the rate constants for all the aldehydes increase with increase of acid concentration, (Fig 2 presents the η vs log i plots of benzaldehyde in HCl used for the determination of ionic exchange current density values and Tafel slopes). The difference in behaviour in the rate constants values in the two techniques may be attributed to the interference of hydrogen evolution possible in controlled potential electrolysis in acid
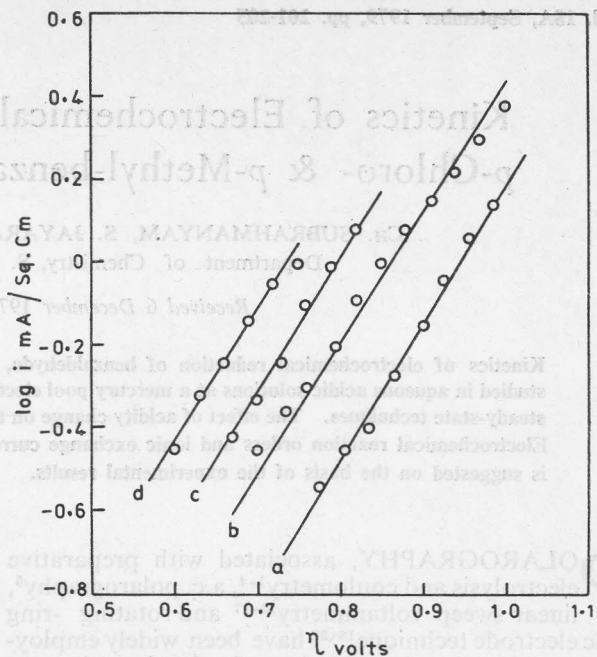
concentration greater than 1 molar. The decrease of current efficiency beyond 1 molar acid concentration also supports this view. (It may be noted that molar HCl and 1 molar H_2SO_2 have approximately same acidity function). Current efficiencies [= $(Q_0/Q_e)/100$] were measured at all acid concentrations (Q_0 = coulombs obtained, Q_e = coulombs expected.)

The variation of the rate constants with Hammett acidity function H_0 (H_0 values from the literature[34] for benzaldehyde shows that the rate increases linearly with a unit slope upto 1 molar acid and thereafter it decreases. Thus the Zucker-Hammett treatment, is not obeyed. Therefore Bunnett's approach has been applied. In the Bunnett type of correlation two different slopes ω_A and ω_B are obtained. In the Bunnet and Olsen type of correlation with acidity function also two different slope values, ϕ_A and ϕ_B are noted. ω_A, ω_B and ϕ_A, ϕ_B values for all the aldehydes are presented in Table 2. The observation of the different slopes is suggestive of the presence of a reaction interfering beyond 1 molar acid concentration.

Figs. 3 and 4 show the UV absorption spectra of the three aldehydes in 1 M HCl (with 25 times dilution of the solutions before and after electrolysis). For identification of the product, benzaldehyde was electrolysed several times under the experimental conditions. After electrolysis, the solid formed in the cathode compartment was taken in ether and the ether extract dried over anhydrous Na_2SO_4. The solid obtained after ether evaporation was recrystallized from CCl_4 three times. The major solid product (TLC pure) was identified as pinacol, m.p. 136-37° (lit 138°); IR 3520 cm^{-1}(OH) and absence of peaks in the carbonyl region. The periodic acid test for solid product indicates that there are two OH groups in the adjacent carbon atoms (Malaprade reaction[35]). This is in agreement with results of other workers[11]. The substituted benzaldehydes also showed similar

TABLE 1 — RATE CONSTANTS (k) AND IONIC EXCHANGE CURRENT DENSITY (i_0) FOR THE ELECTROCHEMICAL REDUCTION OF VARIOUS ALDEHYDES

[Acid] M	HCl		HClO$_4$		H$_2$SO$_4$	
	$k \times 10^{+3}$ sec^{-1} (c.p.e.)	$i_0 \times 10^{+6}$ (A/cm^2) (i-v curves)	$k \times 10^{+3}$ sec^{-1} (c.p.e.)	$i_0 \times 10^{+6}$ (A/cm^2) (i-v curves)	$k \times 10^{+3}$ sec^{-1} (c.p.e.)	$i_0 \times 10^{+6}$ (A/cm^2) (i-v curves)
			BENZALDEHYDE			
0.10	0.38		1.00		0.30	
0.25	0.72		2.24		0.52	
0.50	1.74	1.51	3.81	0.75	0.94	0.90
0.75	2.74		5.00		2.22	
1.00	3.49	2.29	7.76	2.95	3.02	1.58
1.50	2.04		5.00		1.42	
2.00	1.20	3.24	3.16	4.27	0.80	3.70
2.50	0.79		2.00		0.40	
3.00	0.49	5.25	1.39	5.56	0.22	6.29
			p-CHLOROBENZALDEHYDE			
0.10	1.42		1.55		1.74	
0.25	2.13		3.16		2.82	
0.50	4.04	0.37	4.79	0.81	4.57	0.53
0.75	5.75		5.90		5.25	
1.00	7.90	1,41	8.32	1.58	7.60	1.15
1.50	5.12		5.00		5.02	
2.00	3.49	3.16	3.19	2.23	2.24	1.38
2.50	—		1.87		1.01	
3.00	1.10	5.25	1.27	3.98	0.81	2.24
			p-METHYLBENZALDEHYDE			
0.10	0.56		0.91		0.96	
0.25	1.57		1.82		1.42	
0.50	3.51	0.74	3.55	0.32	2.56	0.20
0.75	5.40		4.79		4.00	
1.00	8.02	1.32	6.61	1.26	5.36	1.28
1.50	4.90		3.72		2.82	
2.00	3.20	3.80	2.24	2.82	1.26	2.82
2.50	2.00		1.42		0.69	
3.00	1.63	7.70	0.89	3.82	0.40	4.37

TABLE 2 — SLOPE VALUES OF BUNNETT TYPE OF CORRELATION AND OF BUNNETT AND OLSON TYPE OF CORRELATION

Acid	$\log k$ vs H_0 slope	$\log k + H_0$ vs $\log a_{H_2O}$		$\log k + H_0$ vs $\log C_{H^+} + H_0$	
		A	B	A	B
		BENZALDEHYDE			
HCl	0.96 to —0.95	0	40	0	2.3
HClO$_4$	0.84 to —0.80	—	25	—	3.3
H$_2$SO$_4$	1.10 to —1.00	—	27	—	4.0
		p-METHYLBENZALDEHYDE			
HCl	0.91 to —0.88	0	33	0	4.0
HClO$_4$	0.84 to —0.89	—	28	—	3.3
H$_2$SO$_4$	0.83 to —1.10	0	38	0	3.9
		p-CHLOROBENZALDEHYDE			
HCl	0.87 to —0.94	0	46	—	1.8
HClO$_4$	0.66 to —0.90	—	28	—	3.3
H$_2$SO$_4$	0.77 to —1.05	—	29	—	4.0

behaviour on electroreduction. The CCl$_4$ soluble portion was found to be a mixture of several components (TLC).

The following observations have been considered while arriving at a mechanism for the reduction of the above aldehydes at a Hg electrode:

(i) The number of electrons are found to be 1 upto 1 molar acid through controlled potential coulometry. The deviation of *n*-value from unity after 1 molar acid concentration has been ascribed to the interference by hydrogen evolution.

(ii) The product has been identified as pinacol.

(iii) The cathodic electrochemical reaction order with respect to H$^+$ and aldehydes was found to be one, each. (Figs 5 and 6), suggesting the involvement of one H and one aldehyde molecule in the proton transfer and charge-transfer steps respectively. In the most acidic medium, preprotonation step has been evidenced by earlier workers[2,3,36] before the fast charge-transfer process[16,23,24] Tafel curves were independent of [H$^+$] and their slopes were found to have an average value of 250 mV per decade. The
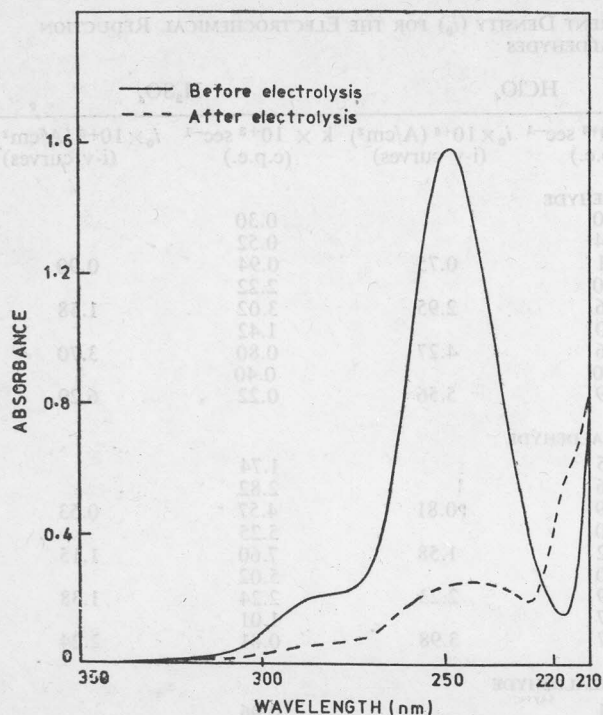
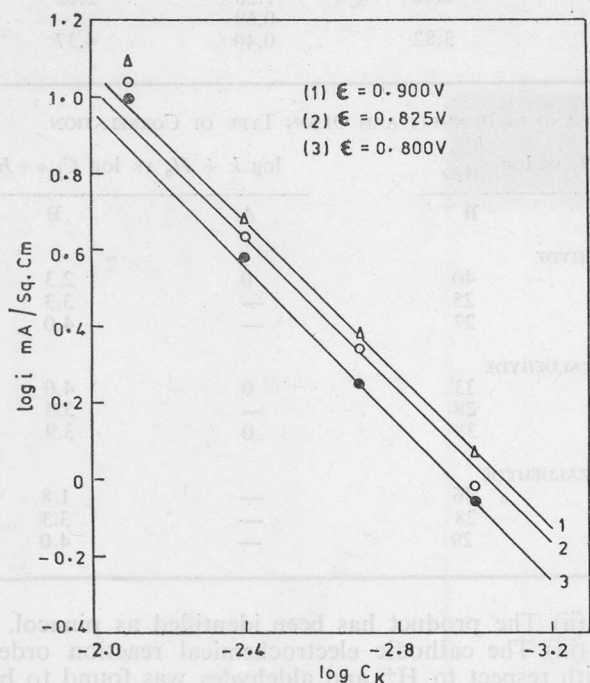Fig 3 —UV absorption spectra of benzaldehyde in 1 M HCl before and after electrolysis.

Fig. 5 — Log i versus log C_{H^+} plots in HCl

Fig. 4 — Log i versus log C_k plots in HCl for p-methyl- and p-chloro-benzaldehydes and benzaldehyde.

Fig 6 — UV spectra of (a) p-chlorobenzaldehyde and (b) p-methylbenzaldehyde in 1 M HCl before (—) and after (- - - -) electrolys.

been suggested to be the rate-determining step as shown by Nadjo and Saveant[14].

(iv) The initial increase in rate constant values suggests the protonated species of aldehydes whose concentration increases with increasing acid concentration as one of the reacting species. This is also in agreement with the order of unity with respect to aldehydes for the cathodic electrochemical reaction.

(v) A comparison of slope values ω and ϕ given in Table 2 with the slope values given by Bunnett[37] indicates the presence of two reaction mechanisms and also that H_2O molecule is not involved in the rate determining step of one mechanism. The deviation in slope is attributed to the interference of hydrogen evolution.

magnitudes of exchange current density values (0.5 to 6.7×10^{-6} A/cm²) and the rate constant values (3×10^{-4} to 7×10^{-3} sec⁻¹) is indicative of a fast charge-transfer process. The dimerisation step has
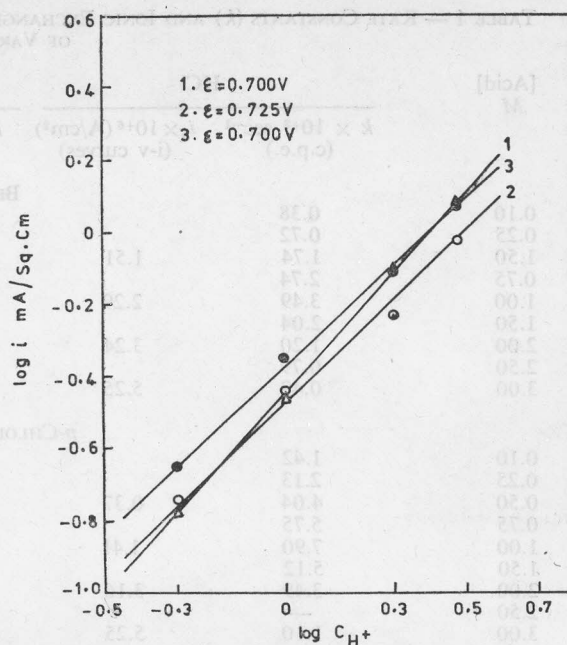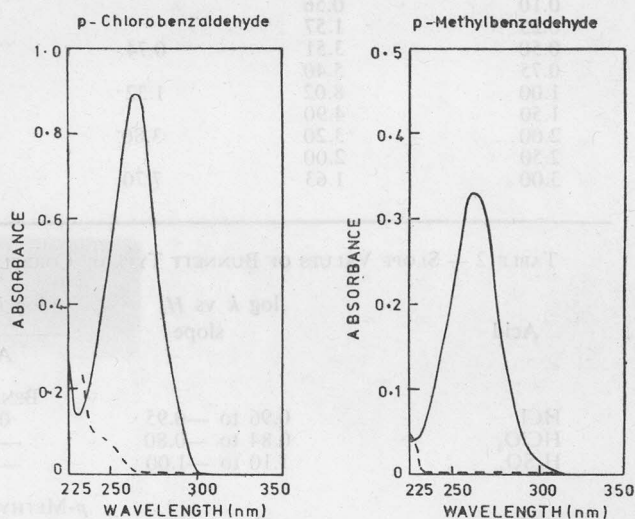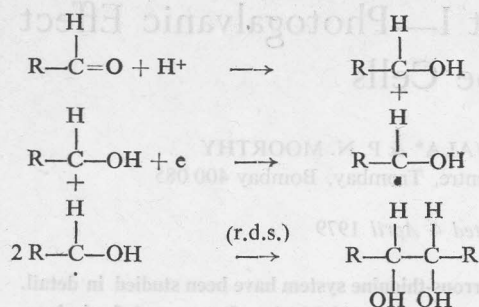
Hence from 0.1 $M \leqslant$ acid $\leqslant 1\ M$, the mechanism shown in Scheme 1 could be assigned for the electrochemical reduction of aldehydes at the Hg electrode.

$$R-\overset{\overset{\displaystyle H}{|}}{C}=O + H^+ \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH + e \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

$$2\ R-\overset{\overset{\displaystyle H}{|}}{C}-OH \xrightarrow{\ \ (r.d.s.)\ \ } R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R$$

$$(R = Ph,\ p\text{-}ClC_6H_4,\ p\text{-}CH_3C_6H_4)$$

Scheme 1

Acknowledgement

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