Electrochemical Reduction of Formaldehyde and Acetaldehyde

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Reducibility of aliphatic aldehydes at DME was recognised quite early [1]. Reduction of formaldehyde and acetaldehyde was also well known [2]. Formaldehyde exists mostly in hydrated form - as methylene glycol. Since only the dehydrated aldehyde form is reducible, the limiting current in DC polarogram is kinetically controlled (by the preceeding dehydration reaction). Acetaldehyde is less hydrated than formaldehyde. So, in this case, the limiting current is partially regulated by the dehydration reaction. The final reduction product in both cases in known to be the corresponding alcohol. Cyclic voltammetry (CV) at gold ratating disc electrode in NaOH medium [3] has been used to determine formaldehyde in melamine - formaldhyde resin. CV of formaldehyde at rotating Pt disc electrode in sulphuric acid medium [4] and at Pt electrode in perchloric acid medium [5] have been reported.

However earlier publications on the effect of pH on reduction mechanism are conflicting [6-10]. The present communication describes the DC, differential pulse polarography (DPP) and CV studies of formaldehyde and acetaldehyde at mercury electrode at different pH.

EXPERIMENTAL

The DC and DPP were carried out using 174-A Polarographic analyzer (EG and G, PARC) with droping mercury electrode (DME), saturated calomel electrode (SCE) and Pt wire electrode assembly. CV was carried out using CV - 27 Voltammograph (BAS) with a hanging mercury drop electrode (HMDE), Ag-AgCl and Pt wire electrode system.

Experiments were carried out using lithium chloride as supporting electrolyte. Acetate and phosphate buffers were used to maintain the pH. Standard formaldehyde solution was prepared from commercial 37% solution. Acetaldehyde sample was further purified by fractionation through an efficient column having indentations; distillate was collected in an ice jacketed receiver. All other chemicals were of AnalaR grade.

Nitrogen gas, was purified by bubbling through vanadous chloride scrubbing solution and used for deaeration of test solution.

RESULTS AND DISCUSSION

In acidic medium, polarographic

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reduction wave (of both formaldehyde and acetaldehyde) merged with that of hydrogen evolution. So studies were restricted to media above pH 7.

DPP studies show that formaldehyde is reduced in a single reduction step beyond -1.4 V *vs* SCE (Table 1). Current increased with pH. The dehydration reaction is base catalysed and the wave in due to the reduction of the dehydrated species, hence this current rise.

A small prewave appeared in DC polarogram of acetaldehyde in the potential region -1.4 to -1.5 V and a main reduction wave in the potential region -1.7 to -1.8 V (vs SCE). The plot of i_l *vs* $\sqrt{h}$ for the main step showed a positive intercept, confirming that the rate of dehydration reaction is partially controlling the limiting current. However the prewave showed linearity in i_l *vs* h plots - suggesting adsorption as the cause of the prewave. This prewave was not reported earlier. DPP and CV curves also revealed the corresponding peak in the same potential region (Fig. 1).

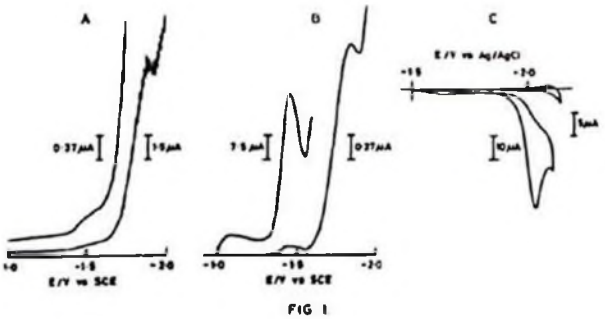


Fig. 1 Polarographic curves of 5 mM acetaldeyde.
A-dc, B-DPP, C-CV;
Phosphate buffer; pH 9.2;
0.2 M LiCl as supporting electrolyte;
scan rate 5 mVs^{-1};
pulse amplitude 50 mV;
drop time 1 sec.

Table 1 includes DPP characteristion of formaldehyde and acetaldehyde. Both peaks of acetaldehyde shift to negative values with pH but they are separated by 0.4 V at all pH values. Peak current of the first was independent of pH but that of main peak decreased, reached a minimum and then increased with pH.

Table 1

DPP characterisatics of formaldehyde and acetadehyde at different pH

pH	Formaldehyde		Acetaldehyde			
	E_{pc}/V	I_{pc}/μA	E_{pc}/V		I_{pc}/μA	
			I peak	II peak	I peak	II peak
7.0	-1.41	0.98	-1.44	-1.83	2.60	72.50
8.0	-1.44	1.28	-1.44	-1.74	2.52	52.85
9.2	-1.46	1.40	-1.45	-1.84	2.61	44.85
10.2	-1.51	2.27	-1.49	-1.82	2.70	39.67
11.0	-1.56	7.30	-1.52	-1.83	2.44	44.25
12.0	-1.62	24.30	-1.53	-1.87	2.12	78.55

To check the reversibility of the reaction, cyclic voltammetric study of the two aldehydes was undertaken. Formaldehyde gave a single cathodic peak in media of pH > 10.0. At lower alkalinity, the reduction was marked by hydrogen evolution. The peak was sharp in medium of pH > 12 and appeared at - 1.89 V *vs* Ag/AgCl electrode. The effect of pH on the cyclic voltammogram of formaldehyde is shown in Fig 2. Peak potential, E_{pc}, shifted towards more negative potential till pH 11.6 and remained constant thereafter. However peak current, I_{pc}, decreased above pH

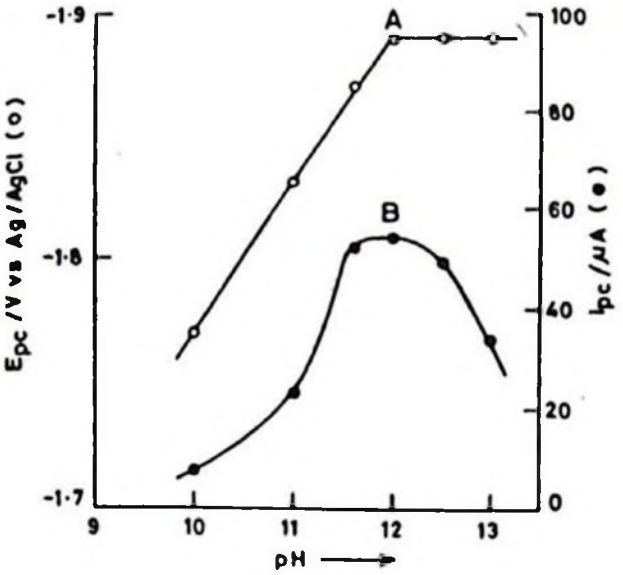


Fig.2 Influence of pH on CV characteristics of formaldehyde
Formaldehyde 1.2 mM;
Phosphate buffer; scan rate mVs^{-1}
Curve A-E_{pc} vs pH;
Curve B i_{pc} vs pH.

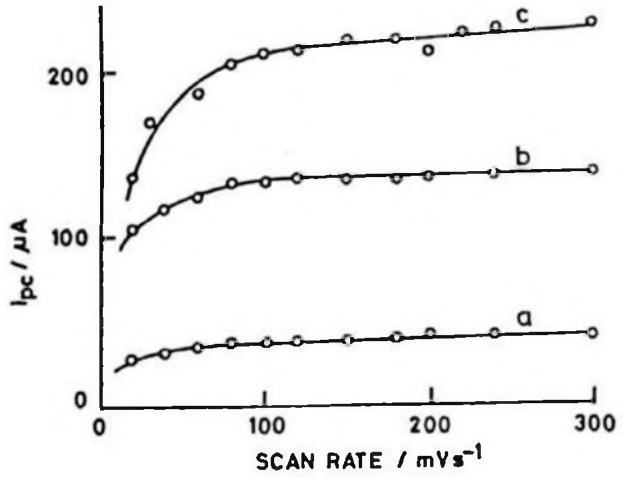


Fig. 3 Influence of scan rate of on cathodic peak current
Phosphate buffer; pH 12.5;
Formaldehyde conen
(a) 0.3 mM (b) 1.0 mm (c) 1.6 mM.

12.2. The peak current of formaldehyde increased slightly with scan rate upto 60 mV/s and thereafter it remained virtually independent of scan rate (Fig 3). This is as expected for a kinetically controlled step.

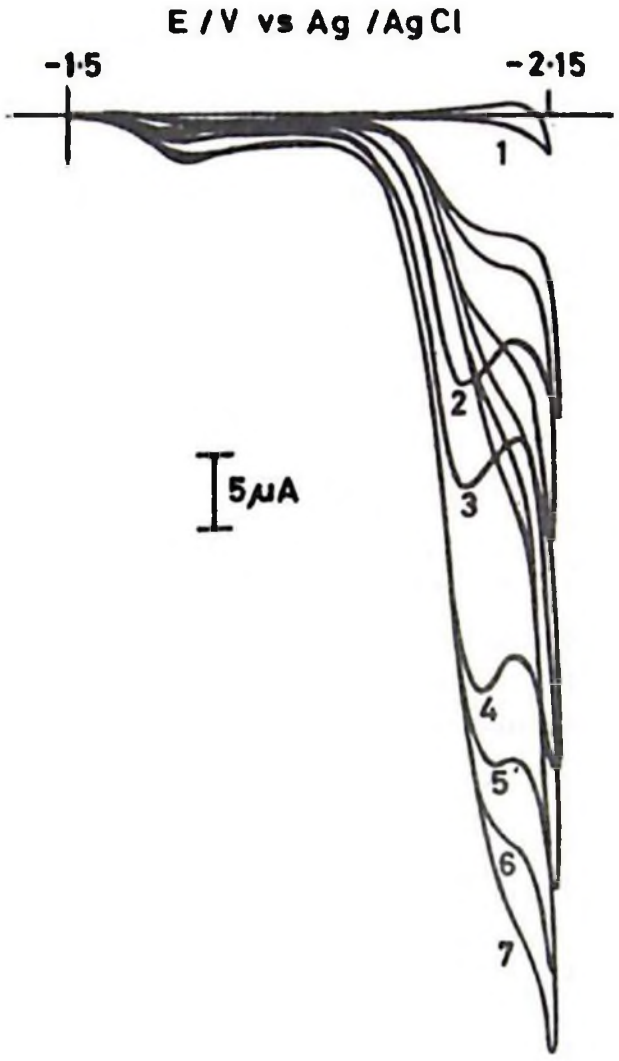
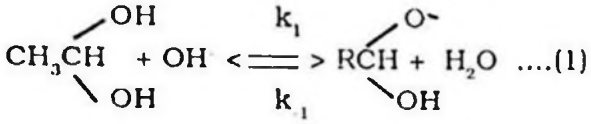


Fig.4: CV curves of acetaldehyde in phosphate buffer of pH 12.5 at different scan rates.
(1) Blank; scan rate 20 mV s-1
(2-7) Acetaldehyde 2.5 mM;
Scan rates 10, 20, 60, 100, 150 and 240 mV.s^{-1}.

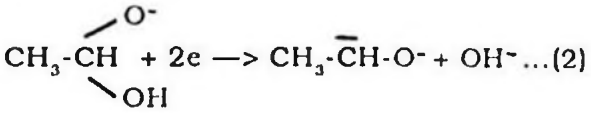
Acetaldehyde in phosphate buffer displayed a small broad peak at potential -1.6 V and main reduction peak at -2.0 V *vs* Ag/AgCl. No corresponding anodic peaks appeared.

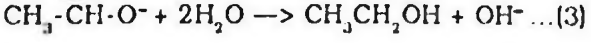
Fig.4 shows that peak current increase with increasing scan rate (υ). In case of formaldehyde, the current was almost independent of scan rate above 60 mV sec^{-1}.

Barns and Zuman [9] have given spectral evidence for involvement of hydrated monoanion RCH(O$^-$)OH as an intermediate in the dehydration process of aliphatic aldehydes including formaldehyde and acetaldehyde.



Clarke and Harrison [7] have shown involvement of CH_2-O- moity in the formaldehyde reduction at pH 13.





Reduction of acetaldehyde occurs at sufficiently negative potential; the electrons could be transferred from hydrated monoanion to give a carbanion moiety (eq. 2). This may remain adsorbed at electrode before it is converted into ethanol (eq.3). This explains the appeareance of prewave in case of acetaldehyde.

ACKNOWLEDGEMENT

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