Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 101, No. 6, December 1989, pp. 473–478.

Electrochemical investigations on β-chlorovinylaldehydes in aprotic media

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MS received 2 August 1989

Abstract. The electrochemical study of β-chlorovinylaldehydes, namely, 4-chloro-3-formyl-2H (1)-benzopyran and β-chlorocinnamaldehyde was carried out in DMF in the presence of 0·1 M NBu_4ClO_4 as the supporting electrolyte. Both the depolarizers give three diffusion-limited polarographic waves and the corresponding cathodic peaks in cyclic voltammetry. Their microcoulometric data indicate a transfer of four-electrons ($n_{app} = 4$) in the electrode process. The macroscale controlled-potential electrolysis of the depolarizers afforded only blackish-brown tarry product. A mechanism is suggested for their reduction in DMF under polarographic conditions.

Keywords. Voltammetric techniques; β-chlorovinylaldehydes; controlled-potential electrolysis; mechanism of electrode process.

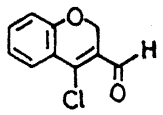
1. Introduction

The electrochemical behaviour of carbonyl compounds has been studied almost as extensively as that of nitro compounds. But, the electrochemical reduction of α,β-unsaturated aldehydes and ketones in protic (Zuman and Michl 1961; Zuman 1967; Ryvolova-Kejharova and Zuman 1969; Zuman and Barnes 1969, 1971; Spritzer and Zuman 1981; Vadaszy and Cover 1974; Mandell *et al* 1971, 1976) and aprotic (Wawzonek and Gundersen 1964; Margaretha and Tissot 1977; Mellor *et al* 1981; Powell and Wightman 1987) media has been found to be more complex than that of saturated carbonyl compounds. Recently, we have noticed that the reduction of various β-chlorovinylaldehydes in buffered aqueous ethanolic solutions at a mercury cathode yielded electrohydrodimerized products in major amounts (Saiganesh *et al* 1989). The present paper deals with a systematic study of the electrochemical reduction of two chlorovinylaldehydes in dimethylformamide (DMF) containing 0·1 M NBu_4ClO_4 as the supporting electrolyte.

2. Experimental

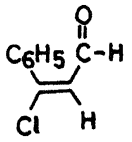
The depolarizers chosen for the present study have structures 1 and 2.

*For correspondence



1

4-Chloro-3-formyl 2H(1)-benzopyran (4-CFB)



2

β-Chlorocinnamaldehyde

The compounds 1 and 2 were prepared according to the literature procedure (Weisenfels and Schunge 1966; Rene and Royer 1975) and were characterized before use. The cell design, instrumentation and various techniques of electrochemical measurements were similar to those described previously (Saiganesh *et al* 1989). DMF (S Merck) was purified according to the literature procedure (Faulkner and Bard 1968; Julliard 1977). Tetrabutylammonium perchlorate (Fluka) was used without further purification. All measurements were carried out at 30°C.

3. Results and discussion

3.1 *Polarography and cyclic voltammetry*

The polarographic measurements on 4-chloro-3-formyl-2H(1)-benzopyran (4-CFB) and β-chlorocinnamaldehyde in DMF in the presence of 0·1 M NBu_4ClO_4 as the supporting electrolyte indicate that both the depolarizers show three diffusion-limited waves at all concentrations. The values of the slopes of the logarithmic plots of $-E_{dme}$ versus $\log(i_1 - i)/i$ confirm the irreversible nature of the polarographic waves of 4-CFB while for β-chlorocinnamaldehyde, the same indicate the irreversible nature of the first and third waves and quasi-reversible nature of the second wave. Figure 1 shows the typical cyclic voltammograms (at 0·300 Vs^{-1} sweep rate) of 4-CFB and β-chlorocinnamaldehyde obtained in DMF in the presence of 0·1 M $NBuClO_4$ as the supporting electrolyte. Both the depolarizers give three cathodic peaks (the third cathodic peak being ill-defined) in the forward scan which correspond to the DC steps and a small anodic peak in the reverse sweep. The constancy in the current function ($i_{p,c}v^{-\frac{1}{2}}$) values with increase in sweep rate (v) for the first two cathodic peaks of 4-CFB and β-chlorocinnamaldehyde as well as the plots of cathodic peak current ($i_{p,c}$) versus square root of the sweep rate passing through the origin indicate the diffusion-limited nature of the peaks.

In the case of 4-CFB, the anodic peak is seen at potentials more positive to the first cathodic peak (figure 1(A)). The voltage excursion and sweep reversal past the first and second cathodic peaks of 4-CFB do not show any anodic peaks. This suggests that the appearance of the anodic peak at more positive potentials is due to the oxidation of the product formed at the end of the third cathodic peak, which is confirmed by potential hold experiments. Holding the potential past the third cathodic peak for a few seconds and thereby reversing the scan increases the peak height of the anodic peak. It may be pointed out that the anodic peak of 4-CFB is observed only at high sweep rates (> 0·100 Vs^{-1}); at low scan rates, the absence of the

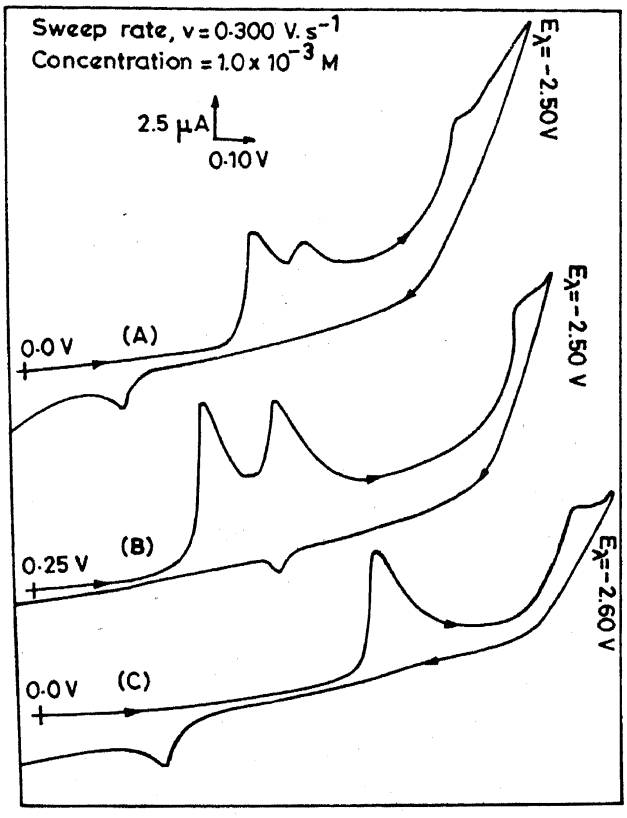


Figure 1. Cyclic voltammograms of 4-CFB (A), β-chlorocinnamaldehyde (B) and 3-FB (C) in DMF (switching potentials, E_λ and starting voltages are indicated in the figure).

anodic peak might be attributed to slow diffusion of the product into the bulk of the solution.

The appearance of the small anodic peak of β-chlorocinnamaldehyde (figure 1(B)) during the reverse scan corresponds to the second cathodic peak. This anodic peak again gives the cathodic peak in the forward scan and in the repeated cycle. Holding the potential past the second cathodic peak of β-chlorocinnamaldehyde and a sweep reversal increases the peak height of the anodic peak, which indicates that the product formed at the end of the second cathodic peak is responsible for the increase in the anodic current. The peak separation (ΔE_p) for the redox species obtained at the end of the second cathodic peak is in the range 0·07–0·09 V and this suggests the quasi-reversible nature of the second cathodic peak. It may be mentioned that the absence of the corresponding anodic peaks for the first and third cathodic peaks of β-chlorocinnamaldehyde indicates the irreversible nature of these peaks.

3.2 *Microcoulometry*

The total number of electrons (n_{app}) transferred at the limiting regions of the polarographic waves of 4-CFB and β-chlorocinnamaldehyde in DMF was obtained from microscale controlled-potential electrolysis (Varkey *et al* 1974) and the results are presented in table 1. It is seen from table 1 that a total of four-electrons ($n_{app} = 4$) are involved in the reduction of 4-CFB and β-chlorocinnamaldehyde in DMF at the

Table 1. Microcoulometric data of 4-CFB (1) and β-chlorocinnamaldehyde (2) in DMF.

Compound	Conc. × 10^3 M	n_{app} values corresponding to the limiting region of		
		Wave I	Wave II[a]	Wave III[b]
1	1·0	2·02	2·98	4·04
	1·5	1·96	2·96	4·02
2	0·5	1·98	3·02	4·02
	1·0	2·02	2·96	4·05

[a] Total of waves I and II; [b] total of waves I, II and III

end of the third wave and the number of electrons corresponding to each reduction step is two, one and one for the waves I, II and III, respectively.

3.3 *Mechanism of the electrode process*

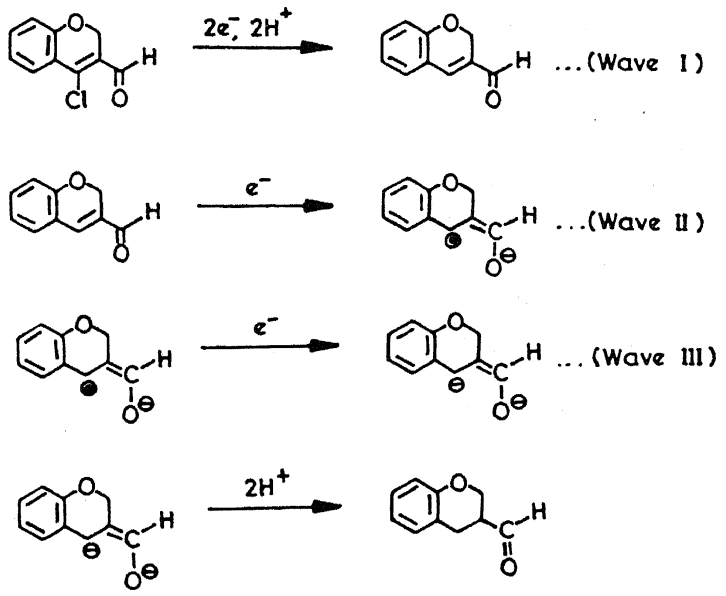
The fact that the first step in the reduction of 4-CFB and β-chlorocinnamaldehyde which might correspond to the reductive fission (or hydrogenolysis) of the carbon–chlorine bond by a two-electron process (*vide* table 1) is supported by Miller's observation on the electrochemical reduction of vinyl bromides (Miller and Rienka 1969). It has been reported by them that the reductive fission of the carbon–bromine bond occurs in preference to the reduction of the carbon–carbon double bond and also that the carbon–halogen bond fission in vinyl halides is more facile if the olefinic carbon bearing the halogen is conjugated. This is confirmed in the present work by independently carrying out the electrochemical reduction of 3-formyl-2H(1)-benzopyran (3-FB, a compound which has no chlorine atom in the 4-position) in DMF under identical conditions. The cyclic voltammogram of 3-FB (figure 1(C)) shows the absence of the more positive first cathodic peak which is observed for 4-CFB (figure 1(A)) and β-chlorocinnamaldehyde (figure 1(B)). Therefore, it is clearly evident that the first polarographic wave/cathodic peak of 4-CFB and β-chlorocinnamaldehyde results from the reductive fission of the carbon–chlorine bond by a two-electron uptake (*vide* table 1) to give 3-FB and cinnamaldehyde, respectively. The second and third single-electron waves/cathodic peaks of the two depolarizers result from the reduction of the carbon–carbon double bond to give the respective saturated aldehydes (Wawzonek and Gundersen 1964; Zimmer *et al* 1971).

Based on the above discussion, a reaction sequence (scheme 1) is proposed for the reduction of 4-CFB in DMF under polarographic conditions. It may be mentioned that scheme 1 is also operative for the reduction of β-chlorocinnamaldehyde in DMF.

The appearance of the anodic peak in the cyclic voltammogram of 4-CFB (figure 1(A)) is attributed to an irreversible oxidation of the saturated aldehyde which is formed at the end of the third cathodic peak.

3.4 *Macroscale controlled-potential electrolysis*

In order to understand and identify the nature of the products obtained in the reduction of 4-CFB and β-chlorocinnamaldehyde, macroscale controlled-potential



Scheme 1.

electrolysis was performed in DMF in the potential range − 1·300 to 2·200 V versus a silver wire electrode using a divided cell. The dark/reddish brown catholyte solution of the depolarizers obtained after electrolysis was worked up and extracted with ether. The ether solution was dried and on evaporation afforded a brown gummy mass which showed several spots in TLC. The proton NMR spectra of the crude products of 4-CFB and β-chlorocinnamaldehyde were highly complex. It may be emphasized that a survey of literature reveals that the macroscale electrolyses of α, β-unsaturated aldehydes in aprotic solvents invariably give a mixture of dimeric and polymeric products (Wawzonek and Gundersen 1964; Zimmer *et al* 1971; Margaretha and Tissot 1978).

Acknowledgement

Financial assistance to one of the authors (RS) from the Department of Science and Technology is gratefully acknowledged.

References

Faulkner L R and Bard A J 1968 *J. Am. Chem. Soc.* **90** 6284
Julliard J 1977 *Pure Appl. Chem.* **49** 885
Mandell L, Day R A Jr, Johnston C and Faulkner J D 1976 *J. Org. Chem.* **41** 2611
Mandell L, Miller D and Day R A Jr 1971 *J. Org. Chem.* **36** 1683
Mandell L, Miller D and Day R A Jr 1976 *J. Org. Chem.* **41** 4087
Margaretha P and Tissot P 1977 *Helv. Chim. Acta* **60** 1472
Margaretha P and Tissot P 1978 *Electrochim. Acta* **23** 1049
Mellor J M, Pons B S and Stibbard J H A 1981 *J. Chem. Soc., Perkin Trans. I* 3092
Miller L L and Rienka E 1969 *J. Org. Chem.* **34** 3359
Powell L A and Wightman R M 1981 *J. Electroanal. Chem.* **117** 321
Rene L and Royer R 1975 *Eur. J. Med. Chem. Chim. Ther.* **10** 72

Ryvolova-Kejharova A and Zuman P 1969 *J. Electroanal. Chem.* **21** 167
Saiganesh R, Balasubramanian K K and Venkatachalam C S 1989 *J. Electroanal. Chem.* **262** 221
Spritzer L and Zuman P 1981 *J. Electroanal. Chem.* **126** 21
Vadaszy R and Cover R E 1974 *J. Electroanal. Chem.* **49** 433
Wawzonek S and Gundersen A 1964 *J. Electrochem. Soc.* **111** 324
Weisenfels M and Schunge H 1966 *Z. Chim.* **6** 471
Zimmer J P, Richards J A, Turner J C and Evans D H 1971 *Anal. Chem.* **43** 1000
Zuman P 1967 *J. Polarograph. Soc.* **13** 53
Zuman P and Barnes D 1969 *Trans. Faraday Soc.* **65** 1668, 1681
Zuman P and Barnes D 1971 *J. Chem. Soc. (B)* 1118
Zuman P and Michl J 1961 *Nature (London)* **192** 655