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ELECTROOXIDATION OF ORGANIC COMPOUNDS IN ACETONITRILE IN THE PRESENCE AND ABSENCE OF FLUORIDE IONS - A COMPARATIVE STUDY

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Electrochemical behaviour of ferrocene, quinhydrone and thioanisole which exhibit reversible, quasi-reversible and irreversible respectively has been compared in acetonitrile in the presence and absence of fluoride ions at three different electrodes namely platinum, glassy carbon and graphite using cyclic voltammetric technique. The voltammetric behaviour of all the three compounds are qualitatively similar on all the three electrodes. In the absence of fluoride ions, the oxidation potentials of all the three compounds are generally independent of electrode materials. In the presence of fluoride ions the electrodes exhibit significant surface effects and the electrode activity is noticeably lower when compared to fluoride ion free medium.

Keywords: Ferrocene, quinhydrone, thioanisole, cyclic voltammetry.

INTRODUCTION

Studies of fluoride films on platinum and carbon electrodes are of great significance from both fundamental and applied angle. Compared to the investigations in molten electrolyte system [1-9], there are very few studies relating to the electrochemical behaviour of platinum (Pt), glassy carbon (GC) and graphite electrodes in fluoride containing non-aqueous media. Fuchigami and Laurent have extensively studied the electrochemical fluorination of organic compounds on Pt electrodes in $Et_3N.3HF/CH_3CN$ medium. [10-14]. Distinct anodic oxidation peaks have been reported on carbon as well as on Pt electrodes for a number of aromatic hydrocarbons in anhydrous HF [15]. Momoto and his co-workers have carried out some detailed investigations on the electrochemical behaviour of Pt electrode in tetraalkylammonium fluoride -nHF system with and without solvents.

However, the electrochemical behaviour in tetrabutylammonium perchlorate (TBAP) and triethylamine $[Et_3N]$-nHF system containing acetonitrile (CH_3CN) solvent have not been reported so far. The present work aims at studying the electrochemical oxidation of some simple organic compounds on three electrodes namely Pt, GC and high purity graphite. The compounds selected are based on their easy oxidisability in aprotic media.

EXPERIMENTAL

Ferrocene, quinhydrone and thioanisole have been obtained from SRL, India. CH_3CN (HPLC grade) was used as the solvent. $Et_3N.3HF$ was prepared by mixing Et_{3N} with anhydrous HF (TANFAC, India) at low temperature.TBAP was prepared and dried in vaccum.

Cyclic Voltammetry was performed as previously described [16]. The working electrode used are of platinum wire, glassy carbon and graphite. The potential of working electrode was mesured using conventional saturated calomel electrode connected to agaragar salt bridge.

RESULTS DISCUSSION

Voltammetric behaviour in acetonitrile containing TBAP

Typical cyclic voltammograms of 2 mM quinhydrone in CH3CN containing 0.05 *M* TBAP at different sweep rates on Pt,GC and graphite electrodes are shown in Figs. 1A,B and C respectively. Quinhydrone gives well defined quasi-reversible voltammetric behaviour on all the three

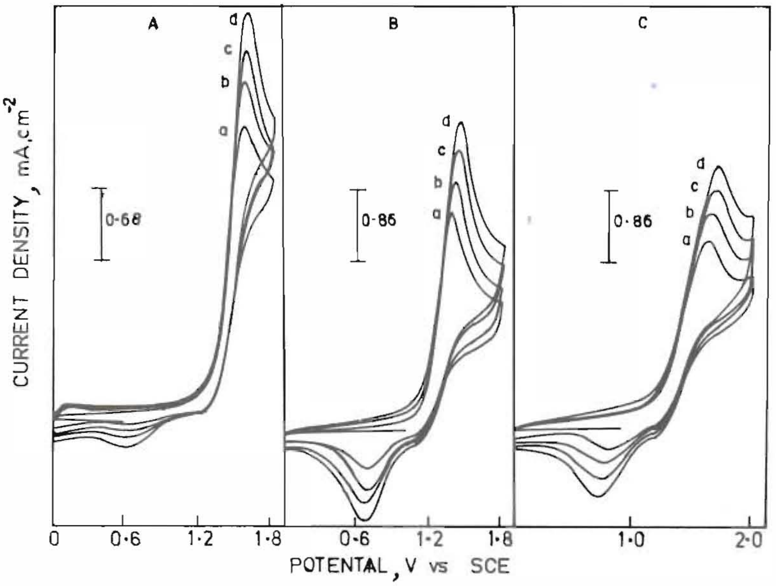

Fig. 1: Effect of sweep rate on the voltammetric behaviour of 2 mM quinhydrone on (A) platinum, (B) GC & (C) graphite electrodes in 0.05 M TBAP/CH$_3$CN medium; v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

electrodes. For comparative purposes at different sweep rates and concentration, i_{pa} values are always tabulated as i_{pa}/C values (mA cm^{-2} mM^{-1}) . In all three subsequent figures also the voltammograms corresponding to Pt, GC and graphite electrodes are given in the same figures A,B & C respectively. The peak current values increase with sweep rate and concentration of quinhydrone on all the three electrodes. The anodic peak potential also shifts to more positive values with concentration. The voltammograms are similar on all the three electrodes. Voltammetric behaviour of ferrocene on Pt, GC and graphite electrodes are compared in Fig. 2. Ferrocene exihibits a much more reversible behaviour when compared to quinhydrone. The anodic and cathodic peaks appear much closer. The anodic peak currents are also generally equal to cathodic peak currents. The voltammetric peak currents increase with increase in sweep rates (Fig.2).

The effect of concentration on the voltammetric behaviour of ferrocene at a sweep rate of 40 mVs^{-1} on all the three electrodes was also compared. The peak currents increase with ferrocene concentration on all the three electrodes. The peak separation ΔE_n therefore increases with concentration

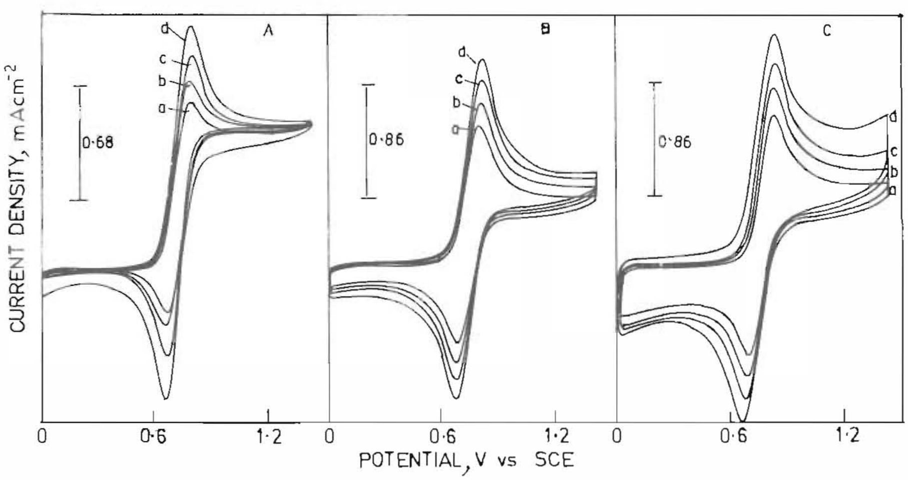

Fig. 2: Effect of sweep rate on the voltammetric behaviour of 2 mM ferrocene on (A) platinum (B) GC & (C) graphite electrodes in 0.05 M TBAP/CH$_3$CN medium, v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

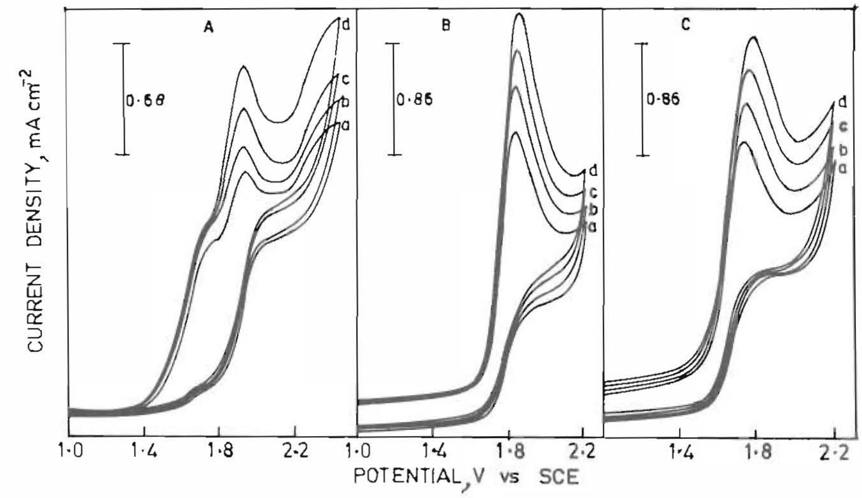

Fig. 3: Effect of sweep rate on the voltammetric behaviour of 2 mM thioanisole on (A) platinum (B) GC and (C) graphite electrodes in 0.05 M TBAP/CH_3CN medium; v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

of ferrocene. On GC and graphite electrodes ΔE_p values were found to be still higher.

Typical cyclic voltammograms of thioanisole on Pt,GC and graphite electrodes at different sweep rates are shown in Fig. 3. Thioanisole gives only anodic peaks. Thioanisole gives three anodic peaks in the wider potential regions on Pt electrodes (Fig. 3A). In the potential region covering 1.0 to 2.2 V Pt alone gives two closely spaced anodic peaks. This is probably connected with the adsorption effect of Pt electrode. GC and graphite electrode gives a single anodic peak.

The effect of concentration of thioanisole on cyclic voltammetric responses were also compared. At higher concentration two closely spaced anodic peaks on Pt were merged together and become a single peak. On all the three electrodes this anoidc peak currents once again increase with increasing concentration of thioanisole.

The voltammetric behaviour of quinhydrone, ferrocene and thioanisole in TBAP/CH_3CN medium at a common sweep rate of 40 mVs^{-1} and concentration of 8 mM are summarised in Table I. for comparison. The anodic peak potential of these compounds do not depend significantly on the electrode material . In general however, the oxidation potential on graphite electrode is slightly higher when compared to Pt electrode. The peak separation values for ferrocene is close to 0.2V on all the three electrodes. Quantitatively, ΔE_p Pt < ΔE_p GC < ΔE_p graphite. The electron transfer rate constant therefore decreases in the above order.

The peak separation value for quinhydrone is much higher around 1.0 V for all the three electrodes. The peak current value i_{pa}/C depends significantly on the compound studied. varied. For the same compound however, i_{pa}/C values are close to each other on all the the three electrodes. A general decreasing trend in the i_{pa}/C value is noticed which is going from Pt through GC to graphite electrode . This is connected with activity of Pt electrode.

Voltammetric behaviour in acetonitrile containing $Et_3N.3HF$

Typical cyclic voltammograms of 2 mM quinhydrone having 0.1 *M* $Et_{N.3HF}/CH_3CN$ at different sweep rates on Pt, GC

TABLE I: Comparison of voltammetric responses in 0.05 *M* TBAP/CH_3CN and 0.1 *M* $Et_3N.3HF/CH_3CN$; Sweep rate: 40 mVs^{-1}; Concentration: 8 mM

Comp-ound	Elect-rode	TBAP/CH_3CN				TEA 3HF/CH_3CN			
		E_{pa}	E_{pc}	ΔE_p	I_{pa}/C	E_{pa}	E_{pc}	ΔE_p	I_{pa}/C
X	Pt	1.72	0.68	1.04	1.03	1.08	---	---	0.61
	GC	1.72	0.81	0.91	0.85	1.36	0.58	0.78	0.41
	GRA	1.80	0.82	0.98	0.71	1.38	0.52	0.86	0.33
Y	Pt	1.06	0.90	0.16	0.31	0.78	0.62	0.16	0.68
	GC	1.10	0.90	0.20	0.38	0.84	0.66	0.18	0.42
	GRA	1.18	0.84	0.34	0.20	0.86	0.66	0.20	0.43
Z	Pt	2.10	---	---	0.91	1.68	---	---	0.86
	GC	2.00	---	---	0.72	1.88	---	---	0.76
	GRA	2.16	---	---	0.62	2.08	---	---	0.66

and graphite electrodes are shown in Figs. 4A, B and C respectively. Quinhydrone gives well defined quasi-reversible voltammetric response for the GC and graphite electrodes. Due to some unknown reasons the cathodic peak in the case of Pt electrode is not observed. The peak currents increase with sweep rates and concentration. The voltammograms also shift towards more positive potential with increase in concentration. The effect is more significant on the graphite electrode when compared to the other electrodes.

Ferrocene exhibits a much more reversible and well defined voltammetric behaviour in $Et_{3N.3HF/AN}$ The voltammetric behaviour is very similar to that of TBAP/AN (Fig.2) of 2 mM ferrocene. Quite sharp anodic and cathodic peak separation values are also low indicating faster electron tranfer. The peak current values also increase with sweep rate and concentration.

Thioanisole exhibits typical irreversible voltammetric behaviour on all the three electrodes. Two distinct anodic peaks are noticed in the potential region of 0.0-2.0 V. The second anodic peak however, is not quite distinct on graphite electrode. The peak currents once again increase with increasing sweep rates and concentration. On the graphite electrode however, the voltammetric responses are poorly defined.

Table I summarises the voltammetric responses of all the three compounds at a common sweep rate of 40 mVs^{-1}. Ferrocene is once again quite easily oxidised on all the three electrodes at the potential of around 0.84 V. The peak separation between the anodic and cathodic peaks remains low at around 0.2 V. This once again suggest that the charge transfer for ferrocene on all the three electrodes is fast. The quinhydrone is oxidised at around 1.0 V on Pt electrode. The oxidation potential is substantially higher at 1.36 V on GC and 1.72 V on graphite electrodes. The peak separation values are also high for GC (0.78 V) and graphite (1.28 V) These factors suggest that the overall electrochemical oxidation rate for quinhydrone is significantly lower on GC and graphite electrodes when compared to Pt electrodes (Table I) .For the oxidation of thioanisole also E_{pa} values on GC and graphite electrodes are significantly higher than Pt elctrodes. This observation once again confirms that the electrochemical oxidation in $Et_3N.3HF/CH_3CN$ medium is more facile on Pt electrode when compared to GC and graphite electrodes.

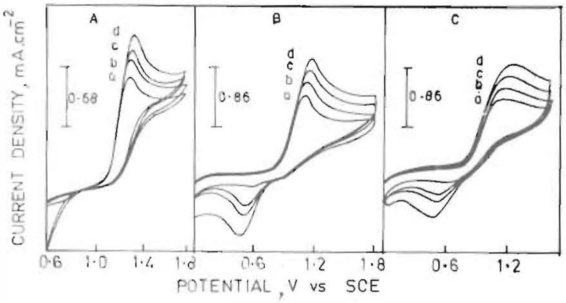

Fig. 4: Effect of sweep rate on the voltammetric behaviour of 2 mM quinhydrone on (A) platinum (B) GC and (C) grpahite electrodes in 0.1 M Et_3N . $3HF/CH_3CN$ medium. v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

The anodic peak current values for these individual compounds vary significantly. For each compound however the anodic peak current value would depend on the activity of the electrode surface. For all the three compounds the peak current values are found to decrease in the order

$$i_{pa}Pt > i_{pa}GC > i_{pa}Graphite.$$

This clearly indicates that the activity of the electrode also decrease in this order in $Et_3N.3HF/CH_3CN$ medium (Table I).

CONCLUSION

On a overall basis the voltammetric behaviour of ferrocene, quinhydrone and thioanisole are qualitatively similar on Pt, GC and graphite electrodes. Hence all the three electrodes can be used in general for analytical purposes in both $TBAP/CH_3CN$ and $Et_3N.3HF/CH_3CN$ media.

In $TBAP/CH_3CN$ media the oxidation peak potentials are generally independent of the electrode material. In this medium the electrode behaves as an inert material and does not exhibit significant surface effect. In $Et_3N.3HF/CH_3CN$ media however, the electrodes exhibit significant surface effects. The anodic oxidation potential E_{pa} generally increases in the order of

$$E_{pa}Pt < E_{pa}GC < E_{pa}\ Graphite$$

The charge transfer kinetics as measured by ΔE_p values also seemed to depend upon the medium. In TBAP/AN media ΔE_p is around 0.2 V for ferrocene and 0.9 V for quinhydrone on all the three electrodes. In $Et_3N.3HF/CH_3CN$ media ΔE_p values for quinhydrone is for example 0.66 V for GCE and 1.14 V for graphite.

The electrode activity as measured by the anodic peak current i_{pa} generally decreases in the order

$$i_{pa}Pt > i_{pa}GC > i_{pa}Graphite$$

However, the relative decrease in $Et_3N.3HF/CH_3CN$ is considerably higher when compared to the decrease in $TBAP/CH_3CN$ medium. This suggests that the electrode activity in $Et_3N.3HF/CH_3CN$ is noticeably lower when compared to $TBAP/CH_3CN$ medium.

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