

COMPARISON OF ELECTROOXIDATION OF ORGANIC COMPOUNDS IN TRIETHYLAMINE - TRIS HYDROGEN FLUORIDE IN PRESENCE AND ABSENCE OF ACETONITRILE

V SURYANARAYANAN, R RAVISANKAR AND M NOEL

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

The electrochemical oxidation of ferrocene, quinhydrone and thioanisole on platinum, glassy carbon and graphite electrodes were compared using cyclic voltammetry in $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium in the absence and presence of solvent CH_3CN . All the three organic compounds show qualitatively similar responses on all the three electrodes as long as their stability is not affected by the medium. In general electron transfer rate appears to be higher in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ when compared to $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ system. Carbon electrodes also exhibit slight surface roughening in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium.

Keywords: Electrooxidation, organic compounds, cyclic voltammetry

INTRODUCTION

Platinum and compact carbon exhibit high corrosion resistance in anhydrous HF (AHF) [1]. These are the electrode of choice in selective electrochemical fluorination and fluorine generation in liquid HF. Most of basic studies on these electrodes in fluoride media are aimed at understanding the mechanism of industrially important electrochemical fluorination processes [2-5]. Fuchigami and Laurent have extensively studied the selective fluorination of organic compounds on Pt electrodes in $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium [6-10]. Carbon electrodes are also interchangeably used in place of Pt electrodes in some recent synthetic works [11-13].

However, the electrochemical behaviour of organic compounds in triethylamine [Et_3N]- $n\text{HF}$ system with and without solvents have not been reported so far. The present work aims at studying the electrochemical oxidation of some simple organic compound on three electrodes namely platinum, glassy carbon (GC) and high purity graphite. The compounds selected are based on their easy oxidisability in aprotic media. The electrochemical oxidation of these compounds has been carried out in $\text{Et}_3\text{N} \cdot 3\text{HF}$ in absence and presence of the solvents, CH_3CN .

EXPERIMENTAL

Ferrocene, Quinhydrone and Thioanisole have been obtained from SRL, India. CH_3CN (HPLC grade) was used as the solvent. $\text{Et}_3\text{N} \cdot 3\text{HF}$ was prepared by mixing Et_3N with anhydrous HF (TANFAC, India) at low temperature.

Cyclic voltammetry was performed as previously described [14]. The working electrode used are of platinum wire, glassy carbon (GC) and graphite. The potential of working electrode was measured using conventional saturated calomel electrode connected to agar-agar salt bridge. In the case of $\text{Et}_3\text{N} \cdot 3\text{HF}$ as a supporting electrolyte system, the potentials were measured with reference to quasi-reversible Pt electrode and the potential values were changed accordingly with reference to saturated calomel electrode.

RESULTS AND DISCUSSION

Voltammetric behaviour of $\text{Et}_3\text{N} \cdot 3\text{HF}$ in the presence of acetonitrile

Typical cyclic voltammograms of 2 mM quinhydrone having 0.1 M $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ 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 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 also with concentration. The

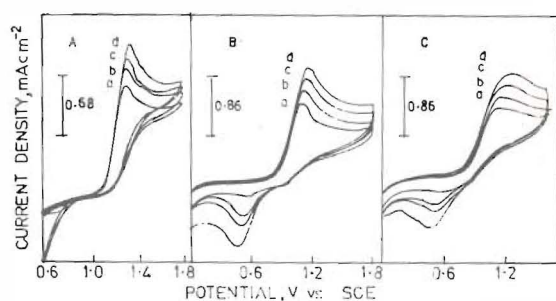


Fig. 1: Effect of sweep rate on the voltammetric behaviour of 2 mM quinhydrone on (A) platinum (B) GC & (C) graphite electrodes in 0.1 M $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

voltammetric responses also shift in the positive direction 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. Typical voltammograms of 2 mM ferrocene on all the three electrodes at different sweep rates are compared in Fig. 2. Quite sharp anodic and cathodic peak separation values are also low indicating faster electron transfer. The peak current values also increase with sweep rate as shown in Fig. 2. The voltammetric peak currents as well peak separation values increase with concentration.

Thioanisole exhibits typical irreversible voltammetric behaviour on all the three electrodes. The voltammetric

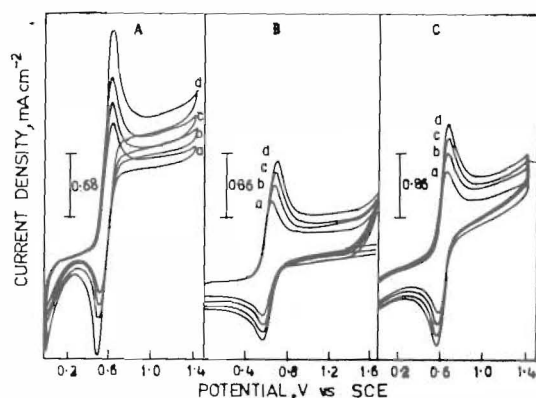


Fig. 2: Effect of sweep rate on the voltammetric behaviour of 2 mM ferrocene on (A) platinum (B) GC & (C) graphite electrodes in 0.1 M $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

behaviour of thioanisole in $\text{TBAP} / \text{CH}_3\text{CN}$ as well as $\text{Et}_3\text{N} \cdot 3\text{HF}$ are very similar [15]. Two distinct anodic peaks are noticed in the potential region of 0-2 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.

Table I summarizes the voltammetric responses of all the three compounds on all the three electrodes at common sweep rate of 40 mVs^{-1} . For comparative purposes at different concentrations, the sweep rate i_{pa} values are always tabulated as i_{pa}/C ($\text{mA cm}^{-2} \text{mM}^{-1}$). Ferrocene is once again quite easily oxidized on 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 suggests that the charge transfer for ferrocene on all the three electrodes is fast. The quinhydrone is oxidized 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. The peak separation values are also high for glassy carbon (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 electrodes. This observation once again confirms that the electrochemical oxidation in $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium is more facile on Pt electrode when compared to GC and graphite electrode.

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.

TABLE I: Comparison of voltammetric responses in 0.1 M $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ and neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ Sweep rate: 40 mVs^{-1} ; Concentration: 8 mM

Compound	Electrode	$\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$				neat $\text{Et}_3\text{N} \cdot 3\text{HF}$			
		E_{pa}	E_{pc}	ΔE_p	i_{pa}/C	E_{pa}	E_{pc}	ΔE_p	i_{pa}/C
X	Pt	1.08	---	---	0.61	0.76	0.39	0.37	1.17
	GC	1.36	0.58	0.78	0.41	0.75	0.49	0.26	0.67
	GRA	1.38	0.52	0.86	0.33	0.75	0.43	0.32	0.34
Y	Pt	0.78	0.62	0.16	0.68	0.40	0.31	0.09	0.45
	GC	0.84	0.66	0.18	0.42	0.42	0.28	0.14	0.41
	GRA	0.86	0.66	0.20	0.43	0.43	0.29	0.14	0.25
Z	Pt	1.68	---	---	0.86	1.09	---	---	0.79
	GC	1.88	---	---	0.76	1.03	---	---	0.71
	GRA	2.08	---	---	0.66	1.07	---	---	0.29

X = Quinhydrone Y = Ferrocene Z = Thioanisole

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

This clearly indicates that the activity of the electrode also decrease in this order in $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium (Table I).

Voltammetric behaviour in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$

There has been very little report so far in the literature relating to the voltammetric behaviour of organic compounds in solvent free neat $\text{Et}_3\text{N} \cdot 3\text{HF}$. This solvent system itself is fairly recent in electrochemistry. In this past few years this solvent-supporting electrolyte system is being evaluated as a medium for selective electrochemical fluorination of organic compounds. In the present study some interesting voltammetric results in this medium on Pt, GC and graphite electrodes are reported.

Typical cyclic voltammograms of quinhydrone in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium on Pt, GC, and graphite electrodes at different sweep rates are presented in Fig. 3. A few precautions and modifications became necessary in these studies. The background currents were always found to be higher in this medium especially for carbon electrodes. To obtain distinct voltammetric peaks a minimum of 25 mM of the reactant was found to be necessary. The salt bridge contents as well as the glass tube are subjected to severe attack in the medium and hence instead of SCE reference, a Pt wire was used as quasi reference electrode. For comparative purposes, the potential scales in figures have been converted into SCE reference scale. Sharp well defined voltammetric peaks are noticed for this compound in this medium. Peak separation values are also significantly low for all the three electrodes as shown in Fig. 3 and Table I.

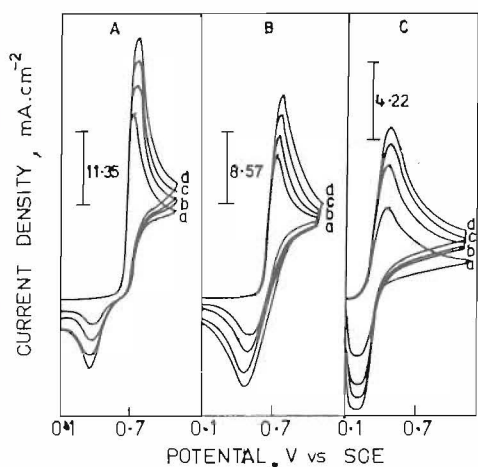


Fig. 3: Effect of sweep rate on the voltammetric behaviour of 2 mM quinhydrone on (A) platinum (B) GC & (C) graphite electrodes in 0.1 M $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium v (mV/sec) (a) 40 (b) 60 (c) 80 and (d) 100

The peak currents increase with the concentration as would be expected. Similar voltammetric responses are obtained for ferrocene in this medium. The ΔE_p values are very low when compared to quinhydrone (Table I).

In $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium thioanisole is found to be oxidized at substantially lower potential. Single irreversible oxidation peaks are observed on all the other electrodes.

The peak current and peak potential data for all the three compounds in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium at common sweep rate of 40 mVs^{-1} are presented in Table.1. Quinhydrone shows excellent voltammetric responses in this medium on all the three electrodes. The anodic peak potential on those electrodes for e.g. is found to be less than 0.4 V on all the three electrode surfaces, compared to more than 0.8 V in $\text{Et}_3\text{N} \cdot \text{HF} / \text{CH}_3\text{CN}$ medium. In the case of ferrocene, the (ΔE_p values in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ are very less compared to $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium. This observation clearly establishes the fact that neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ is a good medium for electrochemical oxidation for compounds which are more difficult to oxidise in other media. This is further confirmed by the observation that the anodic peak potential for thioanisole is also considerably low in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ (Table I).

The anodic peak current values of each organic compound shows a continuously decreasing trend in the order

$$i_{pa} \text{Pt} > i_{pa} \text{GCE} > i_{pa} > \text{graphite}$$

This trend is quite similar to the trend noticed in $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ as well. Quite specifically, the anodic peak current values on graphite electrodes in $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium are considerably lower when compared to the other two electrodes.

Neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ is essentially a highly corroding medium. Hence, a few experiments were carried out to find out if the roughness of the electrodes increased during polarisation in these medium. Pt electrodes do not exhibit any variation of surface area with time. However, as shown in Fig. 4 graphite as well as GC electrodes showed constant increase in anodic oxidation peak currents after each cyclic voltammetric sweep with time interval of 10 minutes each. In the case of GC electrode, the voltammogram stabilised after four voltammetric cycles. In the case of graphite electrode, however, the roughness factor was found to increase continuously without any such limits.

CONCLUSION

Among the three compounds investigated, ferrocene was found to be reversible in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ as well as in

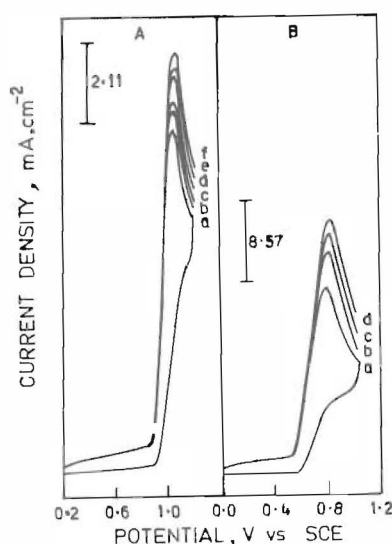


Fig. 4: Effect of sweep rate on the voltammetric behaviour of 25 mM thioanisole on (A) graphite (B) GC & (C) electrodes in $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium v (mV/sec) time interval (minutes) (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 (f) 60

$\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ system on these electrodes. Quinhydrone behaved as quasireversible system and thioanisole behaved as irreversible systems. Quantitatively significant differences are noticed between these two media in the voltammetric features as listed below.

In neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium the oxidation potentials of organic compounds are independent of the electrode material. In $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium, however, the oxidation potentials increase in the order

$$E_{\text{pa}} \text{Pt} > E_{\text{pa}} \text{GC} > E_{\text{pa}} \text{Graphite}$$

The peak current values for individual compounds which is measure of the electrode activity generally decreases in the order

$$i_{\text{pa}} \text{Pt} > i_{\text{pa}} \text{GC} > i_{\text{pa}} > \text{graphite}$$

In neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium, graphite exhibits slight surface roughening over longer periods of polarisation.

E_{pa} values on carbon electrodes in neat $\text{Et}_3\text{N} \cdot 3\text{HF}$ containing very high fluoride ion concentration are indeed significantly lower than $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ which contains relatively low concentration of fluoride ions. This suggests the significant influence of solvents layers on electrode surfaces.

In neat $\text{Et}_3\text{N} \cdot 3\text{HF}$, (ΔE_p values are much smaller on all the three electrodes when compared to $\text{Et}_3\text{N} \cdot 3\text{HF} / \text{CH}_3\text{CN}$ medium. This observation once again confirms the conclusion reached namely higher charge transfer rate in solvent free $\text{Et}_3\text{N} \cdot 3\text{HF}$ medium. Carbon electrodes especially graphite electrode exhibit increase in surface roughness with time in $\text{Et}_3\text{N} \cdot 3\text{HF}$ media.

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