

Effect of Electron - Donating Substituents on Phenol Oxidation

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ABSTRACT

The effect of electron-donating substituents on the oxidation of phenol molecules was studied by cyclic voltammetry. For the considered p-substituted phenol derivatives the reactivity order observed on polycrystalline platinum electrodes was:



For an organic concentration of 0.1M, a linear relationship was found between the current density ($\log i$) and the substituent constant (σ). Literature values for phenol ionization were used.

INTRODUCTION

Electrochemical processes involved in the electrooxidation of organic compounds has become a subject of growing interest due its paramount importance for several different potential applications. The feasibility of an electrochemical technology application for the treatment of organic effluents is influenced by the state of the knowledge of electrocatalysis and the mechanisms of electrochemical reactions of aromatic molecules on solid electrodes [1,2,3].

Phenol and its derivatives are the main compounds in effluents produced by industrial manufactures and are representative of compounds which biodegradability is difficult. Electrodegradation has been attempted by several researchers [1,2,3].

Phenol electrooxidation is possible, converted into CO₂ (complete oxidation) or into less toxic products or/and more easily biodegradable compounds (incomplete oxidation) [3]. The formation and the relative stability of discrete reaction intermediates depends largely on the inductive and polar effects of substituents groups (-R) in the organic. Their presence influences the oxidation mechanism and determines the final reaction products.

The aim of the present work is to investigate the influence of different electron-donating substituents on the oxidability of phenols molecules. Results presented are concerned with p-OH, p-CH₃ and p-OCH₃ substituents on phenol molecules.

EXPERIMENTAL

All experiments were performed in a three electrodes undivided glass cell. A platinum rod was used as a counter electrode and a calomel (SCE) as the reference. All potentials were measured and recorded with respect to SCE. The working electrode, a polycrystalline platinum rod, was subject to an electrochemical pre-treatment using the potential cycling technique between 1400 and -300 mV (scan rate, v , 5 Vs⁻¹), in H₂SO₄ 1M, until the characteristic voltammogram of clean Pt surface was obtained, see Fig 1.

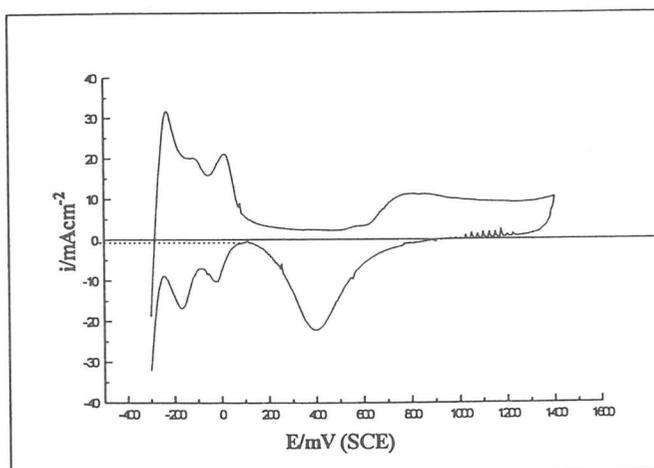


Fig. 1.- Characteristic voltammogram of a clean polycrystalline Platinum surface in 1M H₂SO₄ at room temperature, $v = 5 \text{ Vs}^{-1}$, potential limits: -300 to 1400 mV(SCE).

Voltammograms for Pt in solutions containing organics were run at room temperature at a sweep rate of 50 mVs⁻¹. A potentiostat/galvanostat model 273 A (EG&G) controlled by Research Electrochemical Software (EG&G) was used. The solutions were made up using Analar grade chemicals and distilled water. The area of the electrode used for estimating the current densities values was based on the charge determinations associated to voltammetric peaks for hydrogen adsorption [4,5].

RESULTS

Cyclic voltammograms for polycrystalline platinum electrode in acid medium (1M H₂SO₄) were recorded for each one of the selected substituted phenol compounds at various concentrations (10⁻³-10⁻¹M). Typical curves are presented in fig 2 for an organic concentration of 10⁻¹M.

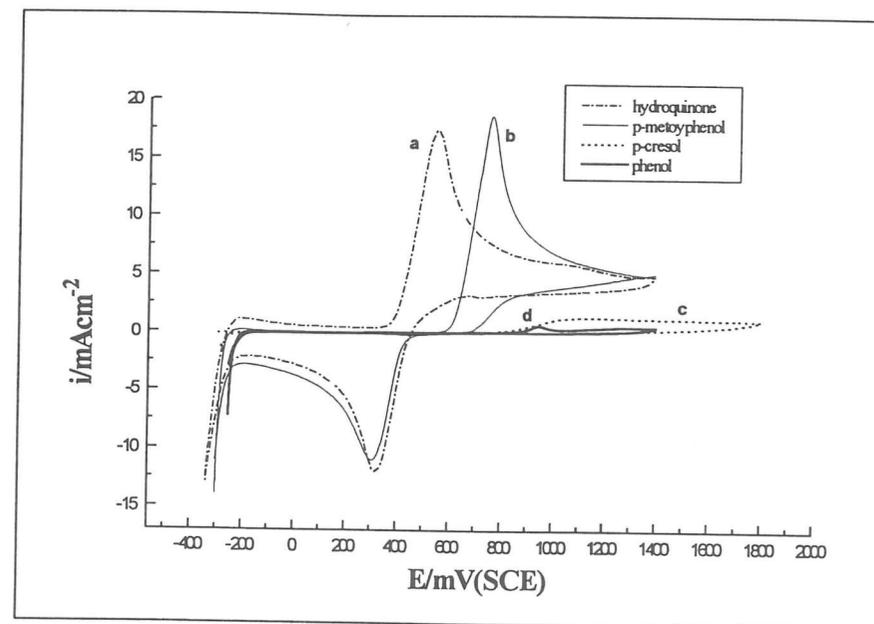


Fig. 2 - Voltammograms of a polycrystalline Pt electrode (50 mV s⁻¹) in acid medium (1M H₂SO₄) with added organics: a) hydroquinone; b)- p-methoxyphenol; c) p-cresol; d) phenol.

Hydroquinone and p-methoxyphenol presented well defined current peaks on direct and reverse sweeps. The anodic peak for hydroquinone is located in the potential range where the platinum electrode begins to be oxidised, while for p-methoxyphenol the peak occurs at 796 mV, within the potential region of platinum oxide(600 to 1300 mV(SCE) in Fig. 1).

For phenol and p-cresol very small currents densities were observed at higher potential values. In the latter case, reduction processes are not evident in the reverse scan.

Peak potentials and associated current densities, determined from the corresponding cyclic voltammograms for all phenol derivatives used, are summarised in Table I.

Table I - Anodic and cathodic peak potentials (EpA and EpC) and corresponding current densities (ipA and ipC) for phenol and phenol derivatives, in a 1 M H₂SO₄ solution, obtained at 50 mVs⁻¹.

Organic	EpA/ mV(SCE)	EpC/ mV(SCE)	ΔEp/ mV(SCE)	ipA/ mAcm ⁻²	ipC/ mAcm ⁻²	ipA/ipC
phenol	916	n. m	n.m	0.40	n.m	n.m
p-hydro-quinone	566	319	247	17.45	11.38	1.53
p-metoxi-phenol	796	310	487	18.74	11.01	1.70
p-cresol	1128	n.d	n.m	1.37	n.d	n.m

n.m- not measured
n.d- not detected

The character of the oxidation reactions is complex and irreversible as indicated by the values of ΔEp and |ipA/ipC| [6].

For both, phenol and p-cresol, the formation of a film was observed by the naked eye and confirmed by subsequent sweeps. The formation of a polymeric film has been suggested by other authors [7].

An attempt to quantify the effect of the presence of substituents on the electrochemical oxidation of phenol molecules was made by correlating the peak current density with the electron-donating power of the substituent, that is, the substituent constant (σ_x). The latter values were obtained from the literature for the dissociation of phenol and its monosubstituted derivatives[8]

For the conditions considered, the plot log ip vs σ_x, see Fig.3, exhibits a linear relationship, similar to Hammett's equation established for the reactivity of aromatic molecules. The slope represents the electrochemical reaction constant, ρ, a measure of sensitivity of the reaction process to changes in the substituent. A negative value of the slope suggests that the limiting step of electrochemical oxidation of the studied compounds is an electrophilic substitution [8,9]. In such cases the electroxidation reactions are more easily promoted by substituents possessing high negative values of substituent constant.

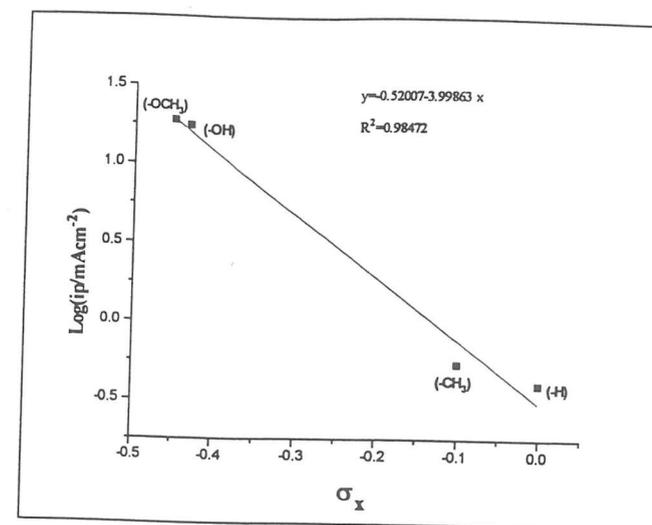


Fig.3 - Representation of log ip versus the substituent constant, σ_x, for phenol and p-substituted phenol derivatives.

CONCLUSIONS

- The electrochemical oxidation of aromatic molecules, in acid medium, on polycrystalline Pt electrodes shows an increase in reactivity according to the order,
phenol (R-H) < cresol (R-CH₃) < hydroquinone (R-OH) < p-metoxi-phenol(R-OCH₃)
- The correlation analysis of the experimental data of electrochemical oxidation rate with the respective substituent constant (σ), exhibited a linear relationship with a negative slope, ρ = - 4, indicated electrophilic attack to the reaction centre.

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