Thermodynamic study of the electrochemical oxidation of some aminophenol derivatives: Experimental and theoretical investigation

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ARTICLE INFO

ABSTRACT

Electrochemical oxidation of some aminophenol derivatives (1–5) has been investigated both experimentally and theoretically. Experimental results were obtained using cyclic voltammetry and controlled potential coulometry. The theoretical results were calculated at DFT (B3LYP and BP86) levels of theory and 6-311 + G (p,d) basis sets. Using a general thermodynamic cycle, the calculated ΔG_{tot} of the oxidation of the studied aminophenol derivatives indicates that thermodynamic is one of the important parameters on the potential oxidation. The obtained results show that electrochemical oxidation potential of 1–5 is directly dependent on the ΔG_{tot} of electrochemical oxidation. In addition in this paper, mechanisms of the electrochemical oxidation of 4-(piperazin-1-yl) phenol (6) in the presence of various nucleophiles was studied in viewpoint of the thermodynamic. Mechanistic study of the electrochemical oxidation of 6 in the presence of different nucleophiles indicates that although the electrochemical oxidations of 6H+ in the presence of different nucleophiles have different mechanisms but proceed in the thermodynamically favored directions.

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1. Introduction

Electrochemical methods are widely applied to the study of the electroactive compounds and were used to obtain thermodynamic and kinetic information [1–9]. Among electrochemical techniques, cyclic voltammetry is a popular technique which is used for electrochemical studies of complex electrode processes [10]. Electrochemical oxidation of aminophenols at various conditions was studied by numerous workers [11–15]. Also electrochemical oxidation of aminophenols in the presence of different nucleophiles indicates that final products were produced via various mechanisms such as EC, ECE, ECEC, ECECCE and ECECEC [16–20]. In these mechanisms, two-electron oxidation of aminophenols is followed by a Michael addition reaction of nucleophile on electrogenerated quinoneimines. The mechanism depends on some parameters such as; nature of nucleophile, electrolysis medium (solvent, acidity or pH) and aminophenol type [21–24]. These prompt us to answer this question that "why the mechanisms of the electrochemical oxidation of aminophenols in the presence of different nucleophiles are so different?". It was reported that the total change in Gibbs free energy (ΔG_{tot}) of the oxidation of intermediates and products is one of the most important parameters influenced on the reaction mechanisms [25]. Therefore in the first part, E_{p0} (the oxidation potential in pH = 0.0) and ΔG_{tot} of the electrochemical oxidation of aminophenol derivatives (1–5) have been calculated from E-pH diagram and computational method, respectively. The results show a good correlation between ΔG_{tot} and E_{p0}. In the second part, electrochemical oxidation of 4-(piperazin-1-yl) phenol (6) has been studied in the presence of p-toluenesulfinic acid (7), 1,2-dimethylindole (8), 4-hydroxycoumarin (9) and 4-hydroxy-1-methyl-2(1H)-quinolone (10) as the nucleophiles. The results show that the electrochemically generated species which are produced during controlled-potential coulometry, depending on the ΔG_{tot} of the electrochemical oxidation, will participate in the electrochemical or chemical following reactions. The total change in Gibbs free energy (ΔG_{tot}) of the electrochemical oxidation of aminophenol derivatives, intermediates and products were calculated at DFT (B3LYP and BP86) levels of theory using 6-311 +G (p,d) basis set according to the Born-Haber cycle.

2. Experimental

2.1. Apparatus and reagents

Cyclic voltammetry was performed using micro Autolab potentiostat/galvanostat. The working electrode used in the

voltammetry experiments was a glassy carbon disc (1.8 mm diameter) and platinum wire was used as the counter electrode. The working electrode used in controlled-potential coulometry was an assembly of four carbon rods (31 cm^2), while a large platinum gauze constituted the counter electrode. The working electrode potentials were measured versus standard Ag/AgCl (all electrodes from AZAR Electrode). All chemicals were reagent-grade materials, from Aldrich and E. Merck. These chemicals were used without further purification. The phosphate buffer solution (H$_3$PO$_4$/NaH$_2$PO$_4$) was prepared by dissolving appropriate amounts of phosphoric acid (H$_3$PO$_4$) and the pH was then adjusted to 2.0 using concentrated sodium hydroxide and the volume was completed to 1.0 L with deionized water (c = 0.2 M). The same procedure was used for preparation of acetate (pH 4–5), H$_3$PO$_4$/NaH$_2$PO$_4$ (pH 3) and NaH$_2$PO$_4$/Na$_2$HPO$_4$ (pH 6.3–8) buffers. All experiments were carried out at room temperature.

2.2. Computational Methods

The geometries of all species in the gas phase were fully optimized at 6–311G+ (p,d) basis sets DFT(B3LYP, BP86) levels of theory using the Gaussian 03 [26]. Vibrational frequency analysis, calculated at the same level of theory, indicates that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. A starting molecular-mechanics structure for the ab initio calculations was obtained using the HyperChem 5.02 program (MM$^+$ method) [27]. To calculate solvation energies, a popular continuum model of solvation, the Conductor-like Polarizable Continuum Model (CPCM) [28] with the setting ICOMP = 0, have been used at the above levels of theory. The optimized atomic radii were invoked via the solvent keyword RADII = UAHF. Then solvation free energies were obtained using the SCFVAC keyword. There are several reported values for Gibbs free energy of H$^+$ at gas phase, ΔG^0(g,H$^+$), and its solvation energy, ΔG^0(s,H$^+$), in solution. In this work the values of -6.28 [29] and -262.5 [30] kcal/mol for latter energies have been used respectively. In addition, based on what was reported by Davis and Fry [31] the value energy "-0.03766 eV" was used for a free electron at 298 K in our calculation (Fig. 1).

3. Results and discussion

3.1. Voltammetric studies

Fig. 2 shows the cyclic voltammogram (CV) of 4-methyle aminophenol (1) (1.0 mM) in aqueous acetate buffer solution (c = 0.2 M, pH = 5.0). The CV shows an anodic peak (A$_1$) in the positive-going scan and a cathodic counterpart peak (C$_1$) in the negative-going scan which correspond to the transformation of 1 to p-benzoquinonimine (1ox) and vice-versa within a two electron process (Scheme 1) [23,24].
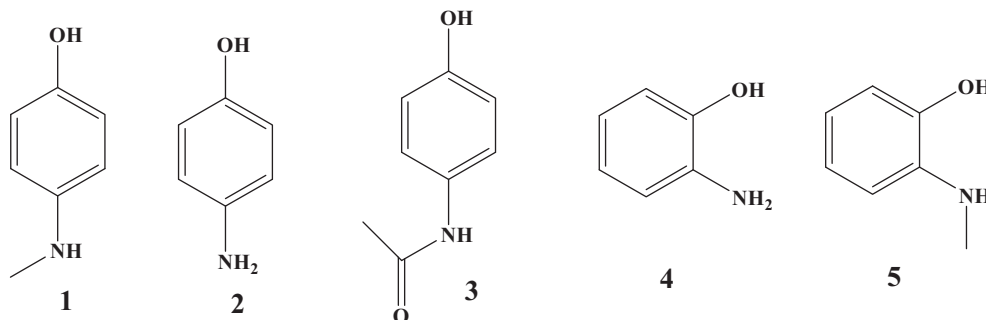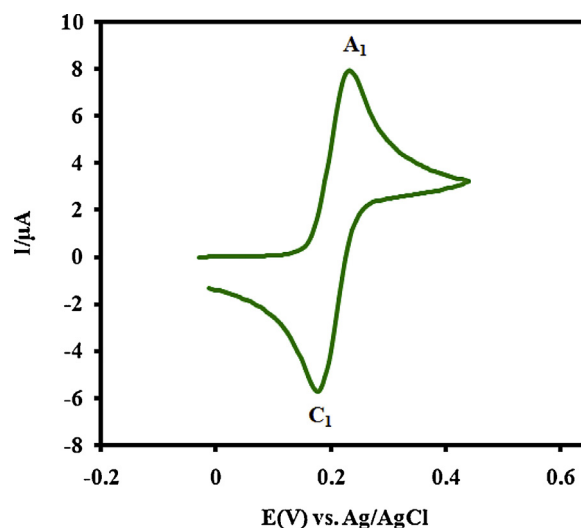

Fig. 2. Cyclic voltammograms of 1.0 mM 4-methylaminophenol (**1**) at a glassy carbon electrode in acetate buffer solution (c = 0.2 M, pH = 5.0). Scan rate: 50 mV s^{-1}; t = 25 °C.

The electrochemical behavior of 1 (1.0 mM) was studied in aqueous solution at various pH values. It was found that the potential of peak A$_1$ (E$_{pA1}$) shifted to the negative potentials by increasing pH. This is expected because of the participation of protons in the oxidation of 1[23]. The anodic peak potential (E$_{pA1}$), is given by:

$$E_{pA1} = E_{p0} - \left(\frac{2.303mRT}{2F}\right)pH \tag{1}$$

where m is the number of protons involved in the reaction and E_{p0} is the anodic peak potential at pH = 0.0, R is the universal gas constant, T is the temperature (in Kelvin) and F is the Faraday constant. An E-pH diagram is constructed for oxidation of the **1** by plotting the E_{pA1} values as a function of pH (Fig. 3). As can be seen, E_{pA1} is shifted to the negative potentials with the slope of 68 mV/pH. This slope is near the theoretical slope (2.303 mRT/2F) of 59 mV/pH with m = 2. On the basis of the mentioned slope, it can be concluded that the electrode reaction is a two-electron, two-proton process (Scheme 1). In addition, E_{p0} was calculated using intercept of E-pH diagrams (E_{p0} = 0.58 V vs. Ag/AgCl) (Table 1). Similar investigations were also performed for aminophenol derivatives (**2-5**) and their data (E_{p0}) were summarized in Table 1.

Because of the relationship between oxidation potential of a compound and its ΔG_{tot} [25], the effect of ΔG_{tot} on the oxidation potential of aminophenols **1-5** was studied. The relationship between potential and ΔG_{tot} is given by:

Fig. 1. The structure of studied aminophenol derivatives.