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Short Communication

Voltammetric oxidation of naphthalene derivatives

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Abstract

A group of 26 naphthalene derivatives was investigated by cyclic voltammetry on a glassy carbon electrode. The compounds were dissolved in water–acetone (1:1 v/v) mixture to which 0.1 M tetramethylammonium tetrafluoroborate was added, as the supporting electrolyte. The measurements were done at room temperature. Oxidation peak current intensities and potentials were measured, and the numbers of electrons transferred were calculated, using Randles–Ševčik equation. The peak potentials were correlated with the calculated, by AM1 program, energies of the highest occupied molecular orbitals of the compounds studies. The obtained data were tabulated, and cyclic voltammograms of naphthalene and acenaphthene, together with the peak potentials correlation, are shown as figures.

Keywords: Naphthalene derivatives; Acenaphthene; Cyclic voltammetry; Glassy carbon electrode; Electrochemical oxidation; Peak potentials; Numbers of electrons transferred; Radical ions

1. Introduction

Since the beginning of organic chemistry, oxidation reactions played a very important role in establishing structures and chemical properties of organic compounds. As an example, one can mention so called *degradation reactions* of natural products under the influence of strong oxidants, or the application of a *reagent*, i.e. solution of potassium permanganate in diluted sulphuric acid, for the transformation of methyl groups into carboxylic ones.

Voltammetry is a very useful electrochemical technique for studying electro-oxidations, especially in connection with using platinum or glassy carbon electrodes [1]. It has been successfully applied to study various groups of organic compounds, e.g. [2–12]. Naphthalene derivatives are an interesting group of model compounds, which can be studied by voltammetry conducted with a glassy carbon electrode.

2. Experimental

Similarly as in Ref. [2], cyclic voltammetric curves were recorded using Auto-Lab PGST12 instrument (Eco-Cell, Holland). A glassy carbon disk of 3 mm diameter was used as the working electrode, and potentials were measured against 1.0 M KCl Ag/AgCl electrode.

To obtain a sufficient solubility of studied compounds, i.e. 0.001–0.008 M, for voltammetric experiments, a mixed solvent of acetone and water (1:1 v/v) was used. As supporting electrolyte $(CH_3)_4N(BF_4)$ was employed, because it allowed to reach positive potentials up to *c.* 2.2 V. The measurements were conducted at room temperature of *c.* 22 °C.

3. Results and discussion

Examples of voltammetric curves of naphthalene and acenaphthene are shown in Fig. 1. From such curves it is possible to calculate the peak potential, E_p [V]. The measured potential of the peak should be decreased by the ohmic potential loss, ΔE_R [V], which is equal to:

$$\Delta E_p = R \cdot I_p \quad (1)$$

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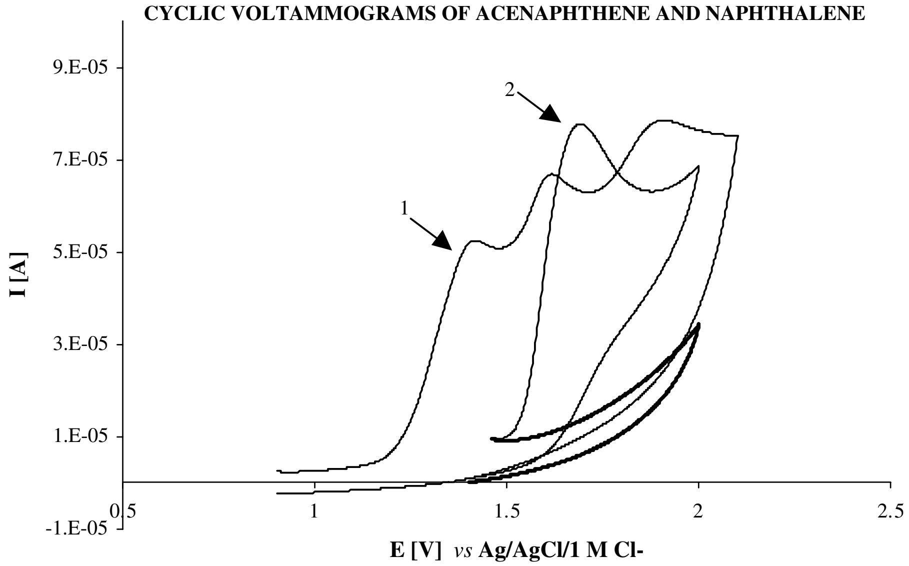

Fig. 1. Voltammetric curves of: 3.0 mM solution of acenaphthene (normal line 1), 3.0 mM naphthalene (normal line 2) and 0.1 M $(CH_3)_4N(BF_4)$ supporting electrolyte in the mixed solvent, acetone–water (1:1 v/v) (solid line). Glassy carbon electrode of 0.3 cm diameter, and the chosen potential rate of 0.02 V/s. A rather low potential rate was chosen to minimize a capacity current and an ohmic potential drop.

where R [Ω] is the ohmic resistance of the cell filled with the supporting electrolyte solution and I_p [A] is the current intensity of the peak. The measured R was *c.* 350 Ω for the applied supporting electrolyte solution of 0.1 M $(CH_3)_4N(BF_4)$ in the mixed solvent of acetone and water (1:1 v/v) at room temperature (*c.* 22 °C). The average range of the measured currents was 10–100 μA, and the corresponding range of the ohmic potential loss was 4–40 mV.

The peak current intensity magnitude can be analyzed by means of the Randles–Ševčik equation [1]:

$$I_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}c \qquad (2)$$

where n is the number of electrons transferred per molecule of substrate, A is the electrode surface area [cm^2], D is the diffusion coefficient of substrate [cm^2/s], v is the voltage sweep rate [V/s], and c is the concentration of substrate [mol/cm^3]. The equation can be rearranged so:

$$\mathrm{CF} = (I_p/Acv^{1/2})^{2/3} = (4.18 \times 10^3)nD^{1/3} = k' \cdot n \qquad (3)$$

where CF is the so called “current function” experimental parameter, proportional to the number of electrons transferred, n, and k' is an experimental proportionality constant, which can be determined for a group of compounds, having similar values of the diffusion coefficient, D. Thus, Eq. (3) can serve to determine the number of electrons transferred in a given process. The constant k' is relatively insensitive to changes in the diffusion coefficient, because the diffusion coefficient is present there in cubic root.

In Table 1 are presented, for 26 studied compounds, the following experimental and theoretical data: the measured peak potentials, the obtained values of the number of electrons transferred, and the calculated energies of the highest occupied molecular orbitals, E_{HOMO}. The numbers of electrons transferred were calculated from experimental peak current intensities and other experimental data, like electrode surface area, $A = 0.07065$ cm^2, substrate concentration, c [mol/cm^3], and the rate of change of potential, v [V/s], using Eq. (3). The constant k', depending on the diffusion coefficient of substrate, has been obtained by comparison with the experimental data in literature, obtained for benzene-1,2-diol (catechol), where the number of electrons transferred on electro-oxidation is known and equal to exactly 2.0 [2,13]. Assuming that the diffusion coefficients of catechol and of the naphthalene derivatives are sufficiently similar, the value of the constant k' to be used at the right-hand side of Eq. (3) is equal to 104.6 for room temperature measurements. The energies of the molecular orbitals have been calculated using the program AM1 of WinMOPAC 2.0 [14].

Another important experimental parameter is the peak potential, E_p [V], which was shown to depend linearly on the computed energy of the highest occupied molecular orbital, E_{HOMO} [eV] for a series of compounds, having a similar mechanism of the electron transfer reaction during electro-oxidations. If there is no correlation between the measured E_p and the calculated E_{HOMO}, then, it may mean that there is a change of the mechanism of the electron transfer reaction [15].

As has been shown earlier, for the most of naphthalene derivatives the prevailing mechanism consists of a formation of a radical cation, as the primary reaction stage:

$$AH_2 - e^- = [AH_2]^{+\cdot} \qquad (4)$$

where AH_2 is the substrate, and $[AH_2]^{+\cdot}$ is the radical cation, which has an unpaired spin and a positive charge at the same time [2,16]. It is assumed that the electron is removed from the highest occupied molecular orbital of E_{HOMO} energy. Thus, the energy of this orbital should