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Does Electro-Oxidation of 1-Ethylnaphthalene Proceed Similarly as that of 2-Ethylnaphthalene?*

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Electro-oxidation of 1- and 2-ethylnaphthalenes is conducted. Products determined by GC-MS show that ethyl group is attacked in 1-ethylnaphthalene, while two isomeric ethyl-1,4-naphthoquinones are obtained from 2-ethylnaphthalene.

Key words: electro-oxidation, ethylnaphthalenes

Electro-oxidation of organic compounds is interesting in the sense, that it is often difficult to foresee the course of reaction and types of products formed. Although many papers and monographs have been published on this topic, however, the observed reactions and their mechanisms are so diverse, that a further study is required [1].

An interesting feature of electro-oxidation reactions is, that an electron transfer takes place at the electrode, and a radical cation is formed:

$$AH_2 - e^- = (AH_2)^{+\cdot} \qquad (1)$$

Radical cations are known to be unstable, rarely their life-times are a few minutes [2], and more often they are milliseconds [3]. Radical cations can react with Lewis bases, with nucleophiles, and with redox species, which can become oxidized. In a way, radical cations can be characterized as *defective molecules*, which lack by one their full set of electrons. The situation here is similar to that in mass spectroscopy, where energetically active gas-phase radical cations are formed by the electron impact (EI) technique. The routes of fragmentation of radical cations in mass spectroscopy are varied [4]. In the case of radical cations in solution, an important factor is *solvation*, which changes the energy of radical cations, and increases their life-time in comparison with that in high vacuum under mass spectroscopic conditions [5].

The two isomeric ethylnaphthalenes are interesting compounds in the sense that delicate variations in their electronic structures may influence the course of radical

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cation reactions. Although it is difficult to study the course of reactions in a complete way, finding the main differences in reactivity is sufficient for the present study.

Studies of radical cations require special experimental systems, like using special solvents (*e.g.* 1,1,2,3,3,3-hexafluoropropan-2-ol) [6,7], application of fast electrochemical techniques, e.g. cyclic voltammetry with rapid voltage sweep [8], and fast electrolysis with extended-surface electrodes and flow of solution [9]. Theoretical simulations help to optimize the concentration of unstable radical ions generated by electrolysis under batch of flow conditions [10–11].

Organic electrochemistry requires optimization of conditions, such as solvent, supporting electrolyte, concentration of substrate, pH, temperature, charge passed, duration of electrolysis, applied potential, current density and *batch* or *flow* mode of electrolysis. To find the optimal conditions of electrolysis for practical preparations requires, thus, much experimental and theoretical work. Our present paper is a small contribution in this direction.

EXPERIMENTAL

The electrolyses were conducted in a divided cell, having a ceramic membrane, and with a 50 cm^3 electrolyte volume mixed by magnetic stirrer The working electrode was a platinum grid of active wire surface area of *c.* 27 cm^2. The experiments were conducted in a *galvanostatic* mode with electrolytic current of about 110 mA, which corresponds to an average current density of approximately 4 mA/cm^2. The initially ambient temperature of the solution was increased during electrolysis to about 50°C due to Joule heat.

The electrolyzed solution consisted of a 1:1 v/v mixture of acetone and water, and 0.1 M. Na_2SO_4 as the supporting electrolyte. The substrates were 0.01 M., which corresponded to 0.5 mmol (78 mg) of ethylnaphthalenes (M_w = 156.23). Cyclic voltammetry (CV) was performed using the same solvent with 0.1 M. $(CH_3)_4N(BF_4)$ supporting electrolyte, and Auto-Lab PGST12 Eco-Cell (Holland) instrument. Glassy carbon electrode of dia. 3 mm was applied in a Methrom electrolytic cell. The potentials were measured against 1 M. Ag/AgCl reference electrode attached to a salt bridge. The CV experiments were conducted at room temperature ($\approx$ 22°C), and air was not flushed out of the working cell.

The electrolyzed solution also contained 0.02 M. $CoSO_4$, applied as redox mediator. Cobalt(+2) ions were oxidized at the electrode to cobalt(+3) ions, which could oxidize the substrate or intermediate products like, e.g. ethylnaphthols, naphthylethanols in solution. The idea was to intensify the oxidation process of ethylnaphthalenes, in addition to the reaction of the latter at the electrode. It is supposed that ethylnaphthalenes, being bulky molecules, have low diffusion coefficients, leading to slow rate of reaction at the electrode.

The usual duration of electrolysis was 2 to 2.5 hrs, and the average electrolytic current, about 110 mA, and charge passed about 900 C per reaction. In view of the 0.5 mmols of substrate taken to reaction, about 18.5 electrons have been transferred per molecule of substrate. The electrolysis was stopped when TLC analysis of the electrolyzed solution did not show further the spot of unreacted substrate at about R_f = 0.77 (for unsubstituted naphthalene) and R_f = 0.80 (for 1-ethylnaphthalene) in the applied eluent of an 1:10 v/v mixture of ethyl acetate and n-hexane, respectively. Assuming that the average number of electrons accepted per molecule of substrate is 6, leading to naphthoquinone as product, it follows from the above number of 18.5 electrons per molecule of substrate passed through the cell, that current yield is about 32%. It means that the majority (*c.* 70%) of current passed was spent for the evolution of oxygen and hydrogen at the electrodes, and the oxidation of Co(+2).

The reaction mixture was extracted with $CHCl_3$ (3 × 5 ml), the extract was dried with $MgSO_4$ and was subjected to GC-MS determination. The solvent was evaporated and the weight of the dry residue was weighed. Typically, it showed *c.* 8.0% increase of weight, which corresponded to the average addition of 0.78 atoms of oxygen per molecule of substrate taken to reaction. The dry residue was extracted with n-hexane, and the fraction of soluble products constituted approximately 28% of the dry residue. The remaining 72% constituted insoluble, polymeric dark-coloured tars. In the case of electro-oxidation of 2-methylnaphthalene, the main soluble product, separated by flash chromatography on silica gel (grain size 0.063–0.200 mm), was 2-methyl-1,4-naphthoquinone, obtained with *c.* 13.9% overall material yield. The average value of added atoms of oxygen per molecule given above, corrected for the percentage amount of the formed 2-methyl- and 6-methyl-1,4-naphthoquinones, becomes *c.* 0.5. Thus, the formed tars contain on average one oxygen atom per two molecules of 2-ethylnaphthalene.

GC-MS analyses were performed using Hewlett-Packard GCMS system consisting of an HP 5890 II gas chromatograph coupled directly to MSD 5972A mass-sensitive detector, and HP-SM5 capillary column. Mass spectra were identified by comparison with recorded spectra in Computer Data Base. The ions were generated by EI technique.

The chemicals, silica gel for flash chromatography (0.063–0.200 mm grain size) and fluorescent TLC plates of 0.2 mm layer thickness, 60 Å mean pore size, on aluminium sheets, were supplied by Merck. The substrates were used as supplied, as their GC-MS analysis did not show presence of impurities. Solvents used (n-hexane, chloroform and ethyl acetate) were of analytical purity, and water was doubly distilled.

GC-MS identification of the main products:

1. α-Methyl-1-naphthalenemethanol

GC-MS: t_R = 20.94 min, MS m/e (% relative intensity): 172 ($M^{.+}$, 29), 157 (35), 153 (9), 130 (11), 129 (100), 128 (47), 127 (27), 126 (8), 115 (4), 102 (4).

2. 1-(1-Naphthalenyl)-ethanone

GC-MS: t_R = 20.34 min, MS m/e (% relative intensity): 170 ($M^{.+}$, 46), 156 (12), 155 (95), 149 (19), 139 (3), 128 (13), 127 (100), 126 (19), 115 (5), 101 (8).

3. 2-Ethyl-1,4-naphthoquinone

GC-MS: t_R = 22.16 min, MS m/e (% relative intensity): 187 ($M^{.+}$ + 1, 13), 186 ($M^{.+}$, 100), 185 (7), 168 (3), 158 (30), 157 (22), 143 (6), 140 (5), 139 (5), 130 (13), 129 (40), 128 (17), 127 (7), 115 (35), 105 (17), 104 (26), 102 (8), 89 (6), 76 (48).

4. 6-Ethyl-1,4-naphthoquinone

GC-MS: t_R = 22.62 min, MS m/e (% relative intensity): 187 ($M^{.+}$ + 1, 13), 186 ($M^{.+}$, 100), 185 (9), 171 (46), 158 (15), 157 (12), 143 (33), 132 (21), 130 (12), 129 (21), 128 (9), 115 (27), 104 (14), 103 (18), 102 (11), 89 (27), 82 (12), 77 (19).

RESULTS AND DISCUSSION

According to the theory of electroanalysis, the concentration of substrate decays exponentially with time, *i.e.* for substrate concentration (C):

$$C = C_o \exp(-kt) \qquad (2)$$

where C_o is the initial concentration of substrate, k is so called *cell constant*, and t is time. The *cell constant* is expressed by the following formula:

$$k = AD/(\delta V) \qquad (3)$$

where A is the surface area of the electrode, D is the diffusion coefficient, δ is the thickness of the diffusion layer, and V is the volume of solution [12–13]. The ratio of the electrode surface area to the cell volume is called *specific area* (s) of the electrolytic cell:

$$s = A/V \tag{4}$$

and equation (3) can be simplified:

$$k = D\, s/\delta \tag{5}$$

The higher is s, the higher is the rate of the electrolytic process. In present case, $s = 0.54\ \text{cm}^{-1}$, which is a value typical for analytical coulometric cells [14].

The solvent mixture was chosen to obtain a relatively good balance between the conductivity of solution: 4.4 mS for 0.1 M. Na_2SO_4 , and 5.7 mS for 0.1 M. $N(CH_3)_4(BF_4)$ (for comparison – conductivity of distilled water was 4 μS) and solubility of substrates. Too low conductivity of solution or concentration of substrates lead, respectively, to excessive heating of solution or inefficient electrolysis. In a way, the present solution composition resembles a two-phase system: the *neutral* organic solute is predominantly *solvated* by acetone molecules, while the *charged* radical cations, formed according to equation (1), are prevailingly *solvated* by water molecules. Contrary to water, acetone has a very low autoprotolysis constant ($pK_{auto} = 32.5$). Acetone's dipole moment and dielectric constant equal to 2.7 D and 20.6, while those of water are 1.86 D and 78.36, respectively [5].

The immediate hydration of the radical cations formed in the electrode reaction facilitates electro-oxidation of ethylnaphthalenes, which takes place in this electrolytic medium at $E_p = 1.56$ and 1.65 V for 1-ethyl- and 2-ethyl- isomers, respectively [15–16]. The hydration by water molecules also supplies either a *nucleophilic reagent*, or a *base* to react with the radical cation. In the role of *nucleophilic reagent*, water molecule supplies a hydroxy-substituent:

$$2(AH_2)^{+\cdot} + 3H_2O = AH_2 + AH(OH) + 2H_3O^+ \tag{6}$$

and in the role of a *base*, water abstracts protons, and enables formation of dimers:

$$2(AH_2)^{+\cdot} + 2H_2O = HA\text{-}AH + 2H_3O^+ \tag{7}$$

according to so called *Scholl reaction* [17]. Thus, the role of the solvent is highly important for the direction of reactivity of radical cations. In some solvents, which are not good *bases* or *nucleophilic reagents*, like acetonitrile (dipole moment: 3.9 D) – belonging with acetone to the group of *dipolar aprotic solvents* of low protonic availability and electron-pair donor (EPD) properties – it is possible to observe the presence of radical cations by spectrophotometric or ESR techniques [2–3,18].

Reactions (6) and (7) yield two probable final products of electro-oxidations – the reaction (6) may still be followed by 4-electron oxidation step to the respective quinone – however, the reactions need still to be explained by a suitable mechanism. It seems that the main reason for the reactivity of radical cations is their tendency to lose a proton in presence of a basic solvent:

$$(AH_2)^{+\cdot} + H_2O = (AH)^{\cdot} + H_3O^+ \quad (8)$$

The neutral radical on the right-hand side of equation (8) is easily oxidized in the presence of solvent to form a hydrated carbocation:

$$(AH)^{\cdot} - e^- + H_2O = (AH)^+ \ldots H_2O \quad (9)$$

The carbocation is a very *short-lived* species, and becomes hydroxylated in an interaction with an additional water molecule:

$$(AH)^+ \ldots H_2O + H_2O = AH(OH) + H_3O^+ \quad (10)$$

Thus, hydroxylated products are intermediates in the reaction, and an introduction of one hydroxyl group requires a *two-electronic* oxidation. In the case of alkylnaphthalenes, the hydroxyl group can be substituted into the aromatic nucleus or into the alkyl group, depending on which proton dissociates first in the radical cation, according to equation (8).

Judging from the obtained experimental evidence, in the case of 1-ethylnaphthalene, the ethyl group becomes hydroxylated in position vicinal to the aromatic nucleus. Thus, among the products of this oxidation, α-methyl-1-naphthalenemethanol and 1-(1-naphthalenyl)-ethanone have been found by GC-MS. In contrast, 2-ethylnaphthalene gave two main products: *isomeric* 2-ethyl-1,4-naphthoquinone and 6-ethyl-1,4-naphthoquinone.

The D/δ ratio is recognized as the apparent mass transport coefficient of the system, whose magnitude and variation with temperature have been determined from experimental measurements summarized in Table 1. In accordance with the classical theory of the thermal behaviour of liquid electrolyte diffusivity [19] , the linearized regression

$$\ln(Y) = a + b(1000/T);\ a = 15.56;\ b = -4.35 \quad (11)$$

with coefficient of determination $R^2 = 0.93$ seems to indicate a mild dependence of the diffusion layer thickness on temperature. Since order of magnitude $O[D] = 10^{-6}$–10^{-5} cm^2/s and $O[\delta] = 0.01$ cm [20] , the order of magnitude of D/δ agrees with theoretical expectations.

Table 1. Reaction parameters of an experimental run of electro-oxidation of 2-ethylnaphthalene.

Time, t (min)	Substrate conversion	Temperature, T (K)	$10^4D/\delta$ (cm^2/s)*
15	0.2	308	4.59
30	0.4	315	5.25
45	0.6	318	6.23
60	0.8	323	8.28
75	0.9	325	9.47

*Computed as $Y \equiv 10^4D/\delta = 18520 \ln\{1/(1-x)\}/t$ [t]: s; x: fractional substrate conversion.

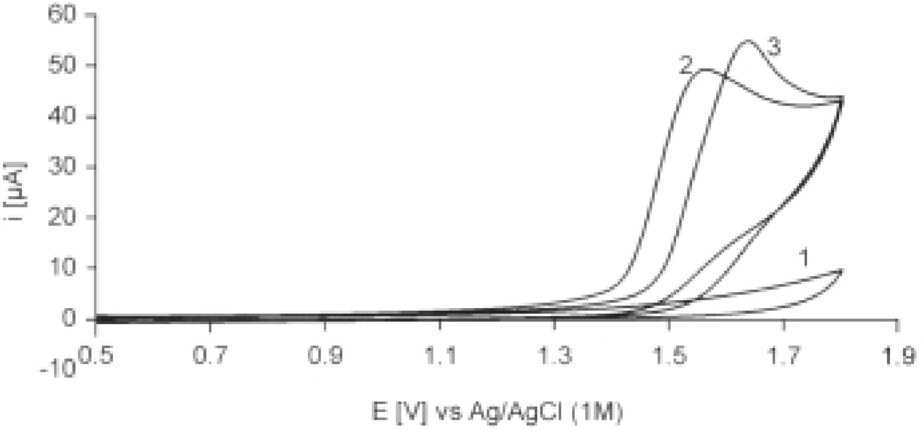

Figure 1. Cyclic voltammetry: curve 1 – supporting electrolyte of 0.1 M $(CH_3)_4N(BF_4)$ in a solvent composed of water and acetone (1:1 v/v); curve 2 – 1.9 mM 1-ethylnaphthalene, 3 – 1.9 mM 2-ethylnaphthalene in the supporting electrolyte solution. Glassy carbon electrode of dia. 3 mm; sweep rate 0.02 V/s.

CONCLUSIONS

The electro-oxidations of ethylnaphthalenes give different types of products, depending on the position of the ethyl group in the aromatic ring. β-Substituted naphthalene gives mainly two isomeric alkyl-p-naphthoquinones and possibly a dimer. α-Substituted naphthalene gives several oxidation products, where oxygen is introduced in the ethyl group, mainly in the α'-position of the alkyl substituent.

Dark-red colored tars, insoluble in n-hexane, constitute about 70% by weight of all the oxidation product. The estimated oxygen content of this unwanted material is *c*. one oxygen atom per two ethylnaphthalene molecular entities. It seems that the formation of the tar is a result of further oxidation of the intermediate product, namely ethylnaphthol:

$$AH(OH) - e^- + H_2O = AH(O\cdot) + H_3O^+ \qquad (12)$$

where AH(O·) is a neutral oxy-radical. This radical may initiate a polymerization involving the substrate, similar radicals, major coproducts, *i.e*. ethylnaphthoquinones, or acetone.

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