Electro-oxidative reactions of naphthalene and alkyl-derivatives

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Naphthalene, methyl-, ethyl-, and several dimethylnaphthalenes were electro-oxidized galvanostatically at Pt-net electrode in 1:1 v/v acetone-water solution, containing 0.1 M Na_2SO_4 as supporting electrolyte and 20 mM $CoSO_4$ as mediator; the average electric charge passed was c. 7 F/mole of substrate per reaction. The products were analyzed by TLC and GC-MS, and separated by column chromatography. Alkyl-substituted quinones were the main products, apart from detected binaphthyls, hydroxy- and carboxyaldehyde derivatives. The mechanism of the oxidation is discussed, which begins with unstable radical cations formed initially at the electrode.

1. INTRODUCTION

Alkylnaphthalenes show a structural feature of having both aromatic and aliphatic groups. Consequently, it is interesting to consider their pattern of behaviour under *strongly* oxidizing conditions of a direct electrooxidation, additionally strengthened by the presence of a mediator Co(+2)/Co(+3) ions in solution. The question requiring an experimental answer concerns the predominant site of the oxidation, i.e. the aromatic or alkyl groups. A similar theme was considered by Schlesener and Kochi, who studied the oxidation of p-methoxytoluene in acetonitrile by means of $Fe(phen)_3^{3+}$ complex in the presence of bases [1]. The present case is further interesting by the two types of

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alkyl substituent positions, α and β. Here, *nucleophilic* or *radical* reactions follow the initial formation of radical cations [2-4].

Electrochemical reactions of organic compounds are studied extensively, because such studies offer perspectives to find new electrosynthetic processes [5]. The radical cations of alkylderivatives of benzene [6], and naphthalene were studied using voltammetric and electron spin resonance methods [7-9]. Spin and charge densities were calculated for methyl- and dimethyl-substituted naphthalene radical cations [10]. Electrochemical oxidation of naphthalene in the presence of nitrite anions was conducted, where radical cations were postulated as intermediates [11].

2. EXPERIMENTAL

A mixture of acetone and water (1 : 1 v/v) was used as solvent, while 0.1 M. Na_2SO_4 or $(CH_3)_4NBF_4$ (in some CV runs) were supporting electrolytes. In most of the electrolytic runs 20 mM. $CoSO_4$ was present as *mediator*.

Cyclic voltammetry (CV) was performed on Pt or glassy carbon electrodes of dia. 1.6 and 3 mm, respectively, using Autolab PGST 12 produced by Eco Chemie (The Netherlands), and the electrolytic cell was from Metrohm. All measurements were carried out at room temperature (22° C).

Micropreparative electrolyses were performed in a divided cell with a glassy frit membrane. The volume of solution in the anodic compartment was 50 ml, and Na_2SO_4 was used as the supporting electrolyte. Both electrodes were made of Pt, the anode being a Pt net of active surface area of *c.* 27 cm^2. The electrolytic current of *c.* 100 to 120 mA intensity was supplied from a galvanostat. Electrolyses were run with 0.5 mmol of substrate (64 to 77 mg depending on mol. wt.). During electrolysis the temperature of the solution in the cell increased up to *c.* 50^oC due to Joule heat. The duration of electrolysis was 2 to 2.5 hrs., and solution was mixed with a magnetic stirrer. Every 15 min. of electrolysis, the composition of the solution was monitored by TLC analysis, and electrolysis was stopped, when substrate was consumed. The average current efficiency was *c.* 30% or less, assuming that naphthoquinones were predominant products in 6-electron oxidation. The electrolyzed solution gradually turned yellow to reddish.

TLC analysis was performed using Merck fluorescent plates and eluent composed of n-hexane and ethyl acetate in a ratio 4 : 1 v/v.

Products were extracted from the electrolyzed solution with chloroform, the extract was dried over anhydrous $MgSO_4$, and solvent evaporated; the dark-red thick oily residue had weight slightly higher (*c.* 8%), than the initial weight of substrate. The residue did not dissolve readily in warm n-hexane. It was subjected to two flash chromatographic separations, using silica gel (Merck,

grain diameter: 0.040–0.063 mm) and eluent composed of a mixture of n-hexane and ethyl acetate (10 : 1 to 2 : 1 v/v). The chromatographic fractions were combined according to their TLC composition, solvent was evaporated, and the residues typically weighed 1 to 8 mg. The residues of yellow oils or needles were analyzed by GC-MS and occasionally NMR. Soluble products typically formed with *c*. 35% overall yield, the remaining matter being a dark tar collected at the head of the chromatographic column.

GC-MS analyses were performed using electron ionization (EI) with either Hewlett-Packard GCMS system containing HP 5890 II gas chromatograph coupled directly to MSD 5972A mass-sensitive detector, or Shimadzu GC-MS QP505OA instrument equipped with NIST 107 and NIST 21 data base.

HRMS spectra were recorded with the aid of AMD-604 double-focussing mass spectrometer.

NMR spectroscopy was performed using Varian 200 or 400 MHz instruments.

Reagents were used as purchased from Merck, Fluka and Sigma-Aldrich.

Identification of products

Trans-cinnamaldehyde was characterized by MS: molecular ion at m/e=132 and daughter lines at 131, 115 and 103, and characteristic ^{1}H NMR (CDCl$_3$, δ, ppm): 6.67 (dd, 1H, J=16.0, 7.6, =C<u>H</u>CHO), 9.81 (d, 1H, J=7.8 Hz, -C<u>H</u>O) in agreement with literature data [12].

2-Ethyl-1,4-naphthoquinone was isolated as yellow needles of m.p. 70–81° C characterized by ^{1}H NMR (CDCl$_3$, δ, ppm): 1.21 (t, J=7.5 Hz; 3H, CH$_3$), 262 (qd, J$_1$=7.4, J$_2$=1.2 Hz; 2H, CH$_2$), 6.80 (t, 1H, 3-CH), 7.73 (m, 2H, 6-CH and 7-CH), 8.09 (m., 2H, 5-CH and 8-CH). MS m/e (relative intensity, %): 186 (M.$^+$, 100), 158 (30), 157 (23), 143 (7), 130 (14), 129 (42), 128 (18), 115 (38). HRMS measured: 186.06898, calculated for C$_{12}$H$_{12}$O$_2$: 186.06808 [13].

6-Ethyl-1,4-naphthoquinone was a yellowish oil characterized by ^{1}H NMR (CDCl$_3$, δ, ppm): 1.30 (t, J=7.8 Hz; 3H, CH$_3$), 2.80 (q, J=7.5 Hz; 2H, CH$_2$), 6.95 (s, 2H, quinoid H), 7.58 (dd, J$_1$=8.0, J$_2$=1.8 Hz; 1H, 7-CH), 7.91 (d, J=1.5 Hz; 1H, 5-ch), 8.01 (d, J=7.9 Hz; 1H, 8-CH) in agreement with literature data [14-15]. MS m/e (relative intensity, %): 186 (M$^+$, 100), 185 (9), 171 (46), 158 (15), 157 (12), 143 (33), 132 (21), 130 (13), 129 (20), 128 (9), 115 (27) [16].

3. RESULTS

Compounds studied are given in Table 1 together with their oxidation peak potentials in CV technique [13,16-17] The initially formed radical cations are unstable, as is evidenced by the irreversibility of the CV oxidation peaks. According to Molecular Orbital theory, radical cations are formed by transferring an electron from the highest occupied molecular orbital (HOMO) of a compound to electrode. Hence, a direct relation can be expected *a priori* between the energy of HOMO and the oxidation peak potential. So far such relations have been found valid especially for aprotic solvents, and are considered to apply *strictly* only, when electrode reaction mechanisms and solvatation effects are similar for a series of compounds [5]. HOMO and a single occupied molecular orbit (SOMO) energies are given in Table 1, as calculated by WinMOPAC program [13,18].

Naphthalene and its alkyl derivatives are electrooxidized at rather high positive potentials, *c*. 1.5–1.8 V *vs.* 1 M. Ag/AgCl electrode. However, naphthols are oxidized at substantially less positive potentials, and dihydroxynaphthalenes at still less positive ones. Considering *micropreparative* electrolysis of naphthalene and its alkyl derivatives, naphthols and dihydroxynaphthalenes are difficult to isolate as intermediates, because of the oxidation potentials difference. The probable final products are naphthoquinones, which are not further oxidized at the available potentials, limited by the decomposition of the solvent.

The CV peak potential of oxidation of Co^{2+} ions according to the electrode reaction:

$$Co^{2+} - e^- \rightarrow Co^{3+} \qquad (1)$$

is shown also. Reaction (1) is the regeneration reaction of the active form of mediator, Co^{3+} ions, which can oxidize intermediate oxidation products, like e.g. naphthols, in solution.

The unpaired electron of the radical cation is located in SOMO orbital, whose energy is lower, than that of HOMO orbital (Table 1). In radical cation there is a spatial distribution of the net electronic charge and unpaired spin density, which influence the *regioselectivity* of the species in *nucleophilic* and *radical* reactions, respectively. Some of the calculated values are given in Table 2 [13]. It follows from the calculated values that positions 1 and 4 (α have higher positive charges, than positions 2 and 3 (β). This indicates a higher probability of a *nucleophilic* attack in positions α than in positions β a conclusion which is borne out by our *micropreparatic* experiments, mentioned earlier.

Tab. 1. Voltammetric peak potentials, calculated HOMO and SOMO orbital energies (taken from refs.[13,17])

No.	Compound	E_p [a]	E_{HOMO} [b]	E_{SOMO} [c]
1	Naphthalene	1.75	-8.711	-10.703
2	1-Methylnaphthalene	1.50[d]	-8.584	-10.471
3	2-Methylnaphthalene	1.61[d]	-8.633	-10.891
4	1-Ethylnaphthalene	1.56[d]	-8.590	-10.458
5	2-Ethylnaphthalene	1.59[d]	-8.563	-10.515
6	1,2-Dimethylnaphthalene	1.60	-8.504	-10.341
7	1,3-Dimethylnaphthalene	1.55	-8.515	-10.325
8	1,4-Dimethylnaphthalene	1.63	-8.456	-10.248
9	2,3-Dimethylnaphthalene	1.46	-8.564	-10.440
10	2,6-Dimethylnaphthalene	1.52	-8.531	-10.342
11	1-Naphthol	0.87[e]	-8.455	-10.366
12	2-Naphthol	0.98[e]	-8.642	-10.439
13	1,4-Naphthalenediol	0.36[d]	-8.211	-9.936
13	1,5-Naphthalenediol	0.69[e]	-8.391	-9.953
14	2,7-Naphtalenediol	0.99[e]	-8.724	-10.465
15	Acenaphthene	1.38[d] 1.58[d] 1.82[d]	-8.495	-10.315
16	Co(+2)	1.62	-	-

a) Peak potentials in V vs. 1 M Ag/AgCl reference electrode. Supporting electrolyte: 0.1 M Na2SO4 , and 1.6 mm dia. Pt electrode, if not stated otherwise.
b) Energy of HOMO of parent hydrocarbon in eV.
c) Energy of SOMO of radical cation of hydrocarbon in eV.
d) Supporting electrolyte: 0.1 M. (CH3)4NBF4 , and 3 mm dia. glassy carbon (GC) electrode.
e) Supporting electrolyte: 0.1 M. (CH3)4NBF4 , and 1.6 mm dia. Pt electrode.

Further, positions having relatively higher unpaired spin density will be sites of a *radical* attack. According to Table 2, there is a positive correlation between the positions of the highest net positive charge and of the highest unpaired spin density. It means that both the *nucleophilic* and *radical* reactions of radical ions lead to substitution in similar sites, which should make some products more probable, than others. For the four radical cations in Table 2, the coefficients of correlation between the unpaired spin densities and net electronic charge are: 0.952, 0.892, 0.967 and 0.815, respectively.

Tab. 2. Calculated unpaired spin densities and net atomic charges of radical cations (taken from ref. [13])

No.	Radical cations of compounds/ Positions	Unpaired spin density	Net atomic charge
1	1-Methylnaphthalene		
	1	0.20	+0.11
	2	0.07	-0.10
	3	0.07	-0.09
	4	0.20	+0.03
	5	0.16	+0.01
	6	0.05	-0.10
	7	0.07	-0.08
	8	0.15	-0.00
2	2-Methylnaphthalene		
	1	0.20	+0.01
	2	0.10	+0.02
	3	0.03	-0.14
	4	0.17	+0.04
	5	0.16	0.00
	6	0.10	-0.06
	7	0.04	-0.12
	8	0.18	+0.03
3	1,2-Dimethylnaphthalene		
	1	0.21	+0.10
	2	0.11	+0.01
	3	0.04	-0.13
	4	0.18	+0.04
	5	0.14	0.00
	6	0.07	-0.08
	7	0.05	-0.10
	8	0.15	0.00
4	1,3-Dimethylnaphthalene		
	1	0.18	+0.11
	2	0.04	-0.14
	3	0.09	+0.01
	4	0.21	+0.01
	5	0.12	+0.01
	6	0.03	-0.12
	7	0.09	-0.06
	8	0.13	-0.02

A salient feature of radical cation reactions is *unselectivity*, depending on distributions of the net electronic charge and unpaired spin density [3,19]. Accordingly, GC-MS is a suitable analytical technique to study such reactions,

where multiple products may form, in addition to a substantial amount of tar (~70%).

The discussion starts with a description of the of electro-oxidation of naphthalene. The main product was 1,4-naphthoquinone detected by MS spectrum. Further, flash chromatography allowed to separate trans-cinnamaldehyde, characterized by MS and NMR spectra (*vide* Experimental Part). The observation of this aldehyde is a proof of an eventual oxidative opening of aromatic ring. Also a trace amount of 1-naphthol was detected by TLC chromatography, as 1-naphthol has a characteristic feature that it decomposes silver salt solution (Tollens' test) used to sprinkle the chromatogram. 1,1'-Binaphthyl was also formed, characterized by MS and NMR spectra. The quantitative ratio of 1,4-naphthoquinone to 1-naphthol to binaphthyl formed was approx. 10 to 2.5 to 0.9 by GC peaks intensity, respectively.

1-Methylnaphthalene gave a variety of products visible in GC-MS analysis. Apparently, some of the products are derived from the oxidation of methyl group, like 1-naphthalenecarboxyaldehyde (GC peak relative intensity 5%). Among the products also 1,4-naphthoquinone (5%) and 2-methyl-1,4--naphthoquinone (vitamin K_3) (2%) were found, which indicates a possible removal of methyl group by oxidation, or its migration, as experienced earlier [21], respectively. The most abundant product was probably 4-methyl-4-hydroxynaphthalen-1(4H)-one (38%), postulated by analogy with reference [21].

2-Methylnaphthalene was electro-oxidized to form vitamin K_3 and 6-methyl-1,4-naphthoquinone in a quantitative ratio of approx. 3 : 1, according to GC-MS analysis. In addition, a formation of four isomers of dimethylbinaphthyl, in decreasing yields with increasing GC retention times, was found by GC-MS analysis. The most abundant isomer was probably 2,2'-dimethyl-1,1'-binaphthyl. The formation ratio of methylquinone to methylbinaphthyl summary fractions was about 5 to 13 by MS peaks intensity, respectively.

1,2-Dimethylnaphthalene gave several identifiable products, the main among them in decreasing amounts were: 3,4-dimethyl-4-hydroxynaphthalen-1(4H)-one (GC relative peak intensity 28%) [21], 1-naphthalene-carboxyaldehyde (12%), 1-(2-methyl-naphthyl)-methanol (6%), and vitamin K_3 (9%).

1,3-Dimethylnaphthalene gave also several products, namely (in decreasing GC peak intensities): probable 2,4-dimethyl-4-hydroxynaphthalen-1(4H)-one (43%) interpreted by analogy with [21], vitamin K_3 (6%), probable 4,2--dimethyl-1-naphthol (4%), and 3,3'4,4'-tetramethyl-(1,1')-binaphthyl (8%) [8,21-22].

1,4-Dimethylnaphthalene gave several products, the most important identified were: 4-methyl-1-naphthalenecarboxyaldehyde (41%), 1-(4--methylnaphthyl)-methanol (14%), and 1,4-naphthalenedicarboxyaldehyde (4%).

2,3-Dimethylnaphthalene gave several products, namely: 2,3-dimethyl-1,4--naphthoquinone (22%), 6,7-dimethyl-1,4-naphthoquinone (5%), and two isomers of tetramethyl-1,1'-binaphthyl, 2,2',3,3'-tetramethyl-1,1'-binaphthyl (7%) and 2,3,6',7'-tetramethyl-1,1'-binaphthyl (5%).

2,6-Dimethylnaphthalne gave 2,6-dimethyl-1,4-naphthoquinone (6%) and two isomers of tetramethyl-1,1'-binaphthyl 5% and 3%, respectively.

1-Ethylnaphthalene gave several products, namely: 1,4-naphthoquinone (8%), 1-(1-naphthalenyl)-ethanone (6%), α-methyl-1-naphthalenemethanol (28%) and a product of molecular peak at m/e = 188, which may be 4-ethyl-4--hydroxynaphthalen-1(4H)-one (37%) (by analogy, see above and ref. [21]). This product could not be isolated by chromatography, instead two chromatographic fractions were separated, which contained three products of molecular peaks at m/e = 186, probably ethylnaphthoquinones, having *para-* or *ortho-*quinone structures, which differ in the relative intensity of the molecular peaks, i.e. *ortho-*quinones have molecular peaks of small intensity. Surprisingly, the most abundant among them is 2-ethyl-1,4-naphthoquinone, an analogous observation, as in the case of the electrooxidation of 1-methylnaphthalene, discussed earlier.

2-Ethylnaphthalene gave two main products, namely: 2-ethyl-1,4--naphthoquinone and 6-ethyl-1,4-naphthoquinone (*vide* Experimental Part). The two products formed in approx. 3:1 quantitative ratio. No GC peak of a diethylbinaphthyl (a dimer) was found.

4. DISCUSSION

The radical cations initially formed in reaction (2) may be oxidized further at the electrode, or by reaction with Co^{3+} mediator, to a dication (*paired-spin*):

$$AH_2 - e^- \rightarrow (AH_2)^{+ \cdot} \qquad (2)$$

and

$$(AH_2)^{+ \cdot} - e^- \rightarrow (AH_2)^{2+} \qquad (3)$$

As the radical cation or dication are charged species, they are preferentially solvated by water molecules, i.e. the polar component of the solvent employed. The hydration may promote a reaction of a proton abstraction, e.g.:

$$(AH_2)^{+ \cdot} \ldots H_2O \rightarrow (AH)^{\cdot} + H_3O^+ \tag{4}$$

where $(AH)^{\cdot}$ is a dehydrocarboradical. Similarly, for doubly hydrated dication:

$$(AH_2)^{2+} \ldots 2H_2O \rightarrow A' + 2H_3O^+ \tag{5}$$

where A' is naphthyne having a triple bond [23]. There may be possible also a sequence of events, where the dehydrocarboradical produced in reaction (4) is oxidized:

$$(AH)^{\cdot} - e^- \rightarrow (AH)^+ \tag{6}$$

The carbocation $(AH)^+$ becomes hydrated, and a *nucleophilic* substitution reaction is possible:

$$(AH)^+ \ldots 2H_2O \rightarrow AH(OH) + H_3O^+ \tag{7}$$

where AH(OH) is a monohydroxylated product. The sequence of reactions (2), (4), (6) and (7) is an example of an ECEC mechanism, where two electrode (E) reactions, (2) and (6), are followed by two chemical (C) ones, (4) and (7). The sequence of reactions (2), (3) and (5) is an example of an EEC mechanism. The hypothetical unstable naphthyne A' may react with molecule of water:

$$A' + H_2O \rightarrow AH(OH) \tag{8}$$

giving a hydroxylated product, like in reaction (7). Although the products of reactions (7) and (8) look the same superficially, they may be structural isomers. The isomeric naphthols or alcohols, represented by the same general formula AH(OH), are electrooxidized further:
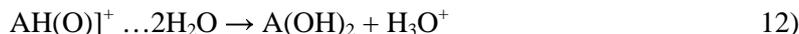
$$AH(OH) - e^- \rightarrow [AH(OH)]^{+ \cdot} \tag{9}$$

forming an unstable radical cation. Further, a proton is abstracted from a hydrated form of radical cation, and an "oxo" radical is formed:

$$[AH(OH)]^{+ \cdot} \ldots H_2O \rightarrow AH(O^{\cdot}) + H_3O^+ \tag{10}$$
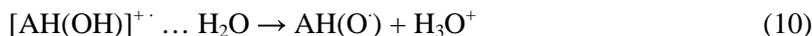
The "oxo" radical may be further oxidized:

$$H(O^{\cdot}) - e^- \rightarrow [AH(O)]^+ \tag{11}$$

to the unstable cation $[AH(O)]^+$, which becomes hydrated, and reacts in a *nucleophilic* mode, giving a diol product:

$$AH(O)]^+ \ldots 2H_2O \rightarrow A(OH)_2 + H_3O^+ \qquad 12)$$

If the first hydroxyl group is introduced in alkyl group, the hydrated "oxo" cation will lead to eventual formation of an aldehyde or ketone:

$$AH(O)]^+ \ldots H_2O \rightarrow A(O) + H_3O^+ \qquad 13)$$

where A(O) denotes an aldehyde of ketone in the alkyl group.

The "oxo" radicals formed in reaction (10) can polymerize with substrate, products or even acetone. The sequence of reactions (2), (3), (5) and (8) represents an EECC mechanism. Other sequences are also thinkable.

The average difference of 1.861 eV (No. of compounds 15, standard deviation 0.148 eV) between the energies of HOMO and SOMO given in Table 1 (E_{HOMO} - E_{SOMO}), indicates that the loss of the second electron according to equation (3) requires a higher potential, than the loss of the first one according to equation (2). This conclusion should, however, be modified, if hydrations of the radical cation and dipositive ion, and the respective enthalpies, play a major role in these reaction mechanisms.

Generally speaking, the possible sequences of reactions, both *electron transfers* at the electrode or in solution (mediator) and chemical reactions in solutions, are *unselective*, i.e. giving a variety of final products, differing in composition, i.e. *the degree of oxidation*, and in structure, i.e. *the structural isomerism*. Due to polymerization reactions, yields of final products of a definite composition and structure are low. The present research effort seems, however, worthwhile to try to understand basic mechanistic schemes of these reaction sequences for planning and optimization of potentially useful electropreparative reactions, like those for the production of vitamin K_3 [24-25].

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