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Reactivity of electrochemically generated radical cations of alkylnaphthalenes interpreted by AM1 calculations

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Abstract—Electro-oxidations of alkylnaphthalenes lead mainly to polymeric products and show a radical cation mechanism. Mechanisms are proposed and discussed based on energetic arguments. Enthalpies of formation and the energies of the HOMO and SOMO, calculated using the AM1 program, are presented. It is shown that the prevailing polymeric products are obtained by way of the intermediate formation of naphthols.

Alkylnaphthalenes form an interesting group of compounds, which are volatile and present in the environment from industrial and combustion (engine) pollution. Their further transformation in solution involves oxid- ation leading mainly to naphtholic and naphthoquinone derivatives. In a recent publication[1] the electro-oxidation of alkylnaphthalenes was studied, and it was shown that the first step of electro-oxidation is the formation of radical cations:

$$AH_2 - e^- = (AH_2)^{+\bullet} \tag{1}$$

Radical cations are present in solution in a solvated form for relatively short periods of time, and react further to produce eventually stable products of various composition, depending on the structure of the substrate. We were interested in trying to assess the reactivity of radical cations based on theoretical arguments and calculations. The situation seemed to be relatively simple, as many of the reacting species are positively charged, and thus, the main 'driving force' for reactivity may be *coulombic* interactions.

As the theoretical tool we adopted the AM1 method of molecular orbital (MO) calculations present in the MOPAC program.[2] The calculated quantities, which are used in the present discussion, are: enthalpies of formation ΔH_f and energies E of the highest occupied molecular orbitals (HOMO) and singly occupied molecular orbitals (SOMO).

The reactivity of radical cations depends also on the composition of the solvent, in particular its nucleophilic and basic properties. In our work a mixed solvent was chosen, composed of water and acetone in a 1:1 v/v ratio. Water is a protic solvent and a donor of hydrogen bonds, while acetone is a dipolar aprotic solvent, which cannot donate hydrogen bonds.[3] As supporting electrolyte, 0.1 M $(CH_3)_4N(BF_4)$ was used. Water is a hard base and a nucleophile, while acetone and the substrates, alkylnaphthalenes, are, respectively, soft electrophile and nucleophiles.[4]

The formation of a radical cation changes the reactivity of alkylnaphthalenes a great deal by adding a (+1) charge to the molecule and transforming it into a hard electrophile. According to the theory of frontier orbitals,[4] a hard nucleophile (water) will react with a hard electrophile (radical cation):

$$(AH_2)^{+\bullet} + nH_2O = [(AH_2)\cdots nH_2O]^{+\bullet} \tag{2}$$

and form a charged activated complex, shown on the right-hand side of Eq. 2 together with associated n water molecules. According to Oyama and co-workers, the formation of an activated complex, as in Eq. 2 for $n = 1$, is rate-limiting for the overall electro-oxidative transformation of aromatic amines.[5] In the activated complex, the positive charge is diffused, and can become

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a target for nucleophilic attack by another water molecule or can react with newly formed and not yet hydrated cation:

$$[(AH_2)\cdots 2H_2O]^{+\bullet} + [(AH_2)\cdots H_2O]^{+\bullet} = AH_2 + AH(OH) + 2H_3O^+ \quad (3)$$

$$[(AH_2)\cdots 2H_2O]^{+\bullet} + (AH_2)^{+\bullet} = AH\text{–}HA + 2H_3O^+ \quad (4)$$

Thus, intermediates in electro-oxidations of alkylnaphthalenes are naphthols and dimers, which have indeed been found (1-naphthol) in the electro-oxidation of naphthalene itself.[1]

Naphthols present another problem of interpretation, because the energies of their HOMOs, from where an electron is taken to form a radical cation, are similar to those of alkylnaphthalenes, however, their oxidation-peak potentials are approximately 0.5 V less positive, than those of simple alkylnaphthalenes, as shown for naphthalene and 1- and 2-naphthols. Dihydroxynaphthalenes show lower positive oxidation-peak potentials, by another 0.1–0.2 V, with respect to those of naphthols.[1]

The relatively large difference between the oxidation-peak potentials of alkylnaphthalenes and naphthols, but not accompanied by a corresponding difference of HOMO energies, indicates that different mechanisms are responsible for the electro-oxidation of alkylnaphthalenes and naphthols.

It was shown that under cyclic voltammetric conditions (CV), the electro-oxidation of alkylnaphthalenes is a two-electron process, and the formation of a radical cation as in Eq. 1 may be followed by a further one-electron oxidation to a dication:

$$(AH_2)^{+\bullet} - e^- = (AH_2)^{2+} \quad (5)$$

The dipositive cation, which is a hard electrophile, may than react with water molecules to form naphthols:

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

This mechanism, although supported by the two-electron height of the oxidation peaks of alkylnaphthalenes,[1] may not be the prevailing one, as we explain below.

It seems that naphthols are also electro-oxidized to a radical cation, however, the radical cation is immediately hydrated, and an hydroxonium ion is lost, leaving a neutral naphthoxy radical:

$$AH(OH) - e^- = [AH(OH)]^{+\bullet} \quad (7)$$

$$[AH(OH)]^{+\bullet} + H_2O = AH(O^\bullet) + H_3O^+ \quad (8)$$

The naphthoxy radicals polymerize, or can be further electro-oxidized; it seems, however, that polymerization is faster.[6]

The dissociation constants at 25 °C of 1-naphthol and 2-naphthol are, respectively, 4.6×10^{-10} and 3.1×10^{-10}.[7] Accordingly, the free energy changes of the dissociation reactions, $\Delta G^\circ = -2.303\,RT\log K_{eq}$, are: 53.3 and 54.3 kJ/mols, respectively, or 0.55 and 0.56 eV/molecule. Assuming that abstraction of an electron from a naphthol molecule is simultaneous with an abstraction of a proton by the solvent, the hypothetical energy supplied to form a radical cation can be decreased by the free energy change of about 0.55 eV, corresponding to the acidic dissociation of naphthols. This energy gain is probably responsible for the difference of CV peak potentials of alkylnaphthalenes and hydroxynaphthalenes.

One can also consider the enthalpies of formation of molecules and radicals participating in the electro-oxidation reactions, calculated by MOPAC and given in Table 1. It follows that the enthalpies of formation of neutral radicals formed by dissociation of a proton from a radical cation, e.g. Eq. 8, are much lower than those of respective radical cations, which strongly favours such reactions.

When a radical cation is formed according to Eq. 1 a single electron occupies the SOMO orbital, which formerly had been a HOMO orbital. The energy of the SOMO becomes lower than that of HOMO, as is shown in Table 1. Thus, the numbers illustrate that the removal of a second electron according to Eq. 5 is energetically more difficult, than of the first one. Additionally, there is a *coulostatic* repulsion between the radical cation and a positively charged electrode. The situation changes, when hydation of the radical cation is possible according to Eq. 2, followed by abstraction of a proton from the hydrated radical cation:

$$[(AH_2)\cdots 2H_2O]^{+\bullet} = [AH_2(OH)]^\bullet + H_3O^+ \quad (9)$$

The neutral radical formed in Eq. 9 can be oxidized at the electrode to form a carbocation:

$$[AH_2(OH)]^\bullet - e^- = [AH_2(OH)]^+ \quad (10)$$

The carbocation is immediately hydrated and loses a proton adopting the aromatic structure of a naphthol:

$$[AH_2(OH)]^+ + H_2O = AH(OH) + H_3O^+ \quad (11)$$

The hydrated radical cation from Eq. 2 can also lose a proton:

$$[(AH_2)\cdots 2H_2O]^{+\bullet} = (AH)^\bullet + H_3O^+\cdots H_2O \quad (12)$$

The neutral radical formed is then oxidized to form a carbocation:

Table 1. Experimental CV peak potentials, calculated HOMO and SOMO energies and enthalpies of formation of chosen naphthalenes, naphthols and their hypothetical transformation products

No.	Compound	CV peak potentials, E_p/V[a]	Energy of HOMO orbital, E_{HOMO}/eV	Energy of SOMO orbital, E_{SOMO}/eV	Enthalpy of formation, ΔH_f/kJ mol^{-1}
1a	Naphthalene	1.69	−8.71		169.3
1b	(Naphthalene)$^{+\bullet}$			−10.70	971.4
2a	1-Naphthol	0.80	−8.46		−13.0
2b	(1-Naphtholate)$^{-}$		−2.94		−128.0
2c	(1-Naphthol)$^{+\bullet}$			−10.37	766.5
2d	1-Naphthoxy radical			−5.22	121.8
2e	1-Napthoxy cation		−14.58		876.6
3a	2-Naphthol	0.94	−8.64		−16.5
3b	(2-Naphtholate)$^{-}$		−3.04		−121.6
3c	(2-Naphthol)$^{+\bullet}$			−10.44	769.1
3d	2-Naphthoxy radical			−5.35	138.5
3e	2-Naphthoxy cation		−14.22		904.9
4a	1-Methylnaphthalene	1.50	−8.55		147.0
4b	(1-Methylnaphthalene)$^{+\bullet}$			−9.20	1226.4
4c	(1-Methylnaphthalene)$^{2+}$		−18.91		2160.7
4d	Naphthalene-1-methylene radical			−4.37	293.7
4e	1-Methylnaphthalene-4-dehydro radical			−4.96	388.6
4f	Naphthalene-1-methylene carbocation		−13.51		974.4
4g	1-Naphthylcarbinol	—	−8.49		−20.55
5a	2-Methylnaphthalene	1.61	−8.63		137.0
5b	(2-Methylnaphthalene)$^{+\bullet}$			−10.55	929.5
5c	Naphthalene-2-methylene radical			−4.36	290.5
5d	2-Methylnaphthalene-1-dehydro radical			−4.95	379.4
5e	2-Methylnaphthalene-4-dehydro radical			−4.96	378.5

[a] CV peak potentials taken from Ref. 1 or measured under conditions described therein.

$$(AH)^{\bullet} - e^{-} = (AH)^{+} \qquad (13)$$

which produces a naphthol molecule on reaction with water:

$$(AH)^{+} + 2H_2O = AH(OH) + H_3O^{+} \qquad (14)$$

A further electro-oxidation of the naphthols, which are intermediate products takes place. Naphthols are more easily electro-oxidized than alkylnaphthalenes, as is shown by their less positive CV peak potentials. According to Eq. 8, naphthols produce naphthoxy radicals on electro-oxidation, which polymerize easily. Hence, in electro-oxidation reactions of alkylnaphthalenes in water–acetone solutions brown polymers are obtained as the main products with yields often exceeding 70%.

References and notes

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