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Cyclic voltammetry for a preliminary study of appropriate electro-synthesis reactions of naphthalene derivatives[1]

Roman E. Sioda, Barbara Frankowska

Department of Analytical Chemistry and Electrochemistry, Institute of Chemistry,
University of Podlasie, Siedlce, Poland

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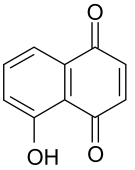
Abstract Cyclic voltammetry on a glassy carbon electrode was used for studies of electro-oxidations of several naphthalene derivatives. The number of electrons participating in the primary reaction at the electrode is derived using the modified *Randles-Ševčik* equation applied to a series of experimental data of peak current intensity *vs.* the potential rate. The mechanism of electro-oxidation of two natural products, juglone and lawsone, is discussed with respect to hydrogen bond formation.

Keywords Electro-organic chemistry; Oxidations; Natural products; Cyclic voltammetry; Hydrogen bond.

Introduction

Compounds, that are biologically active, contain functional groups or double bond configurations, which can be easily electro-oxidized using cyclic voltammetric technique on a glassy carbon electrode. As the result of cyclic voltammetric examination of compounds of interest, one usually obtains a complicated current intensity, I [A], *vs.* applied potential, E [V], curves, which may also change with the applied potential rate, ν [V/s]. From the measured voltammetric curves, one may try to form conclusions concerning the mechanism of the electron transfer at the electrode and of the accompanying solvation, redox, or chemical transformation reactions in solution. Some of the observed reactions and mechanisms may present an interest from the point of view of perspective synthesis studies and even future technological processes.

We present here a similar experimental analysis for two interesting biologically active compounds, namely juglone (5-hydroxy-1,4-naphthoquinone, **1**) and lawsone (2-hydroxy-1,4-naphthoquinone, **2**). Both compounds are strongly coloured, toxic, and are produced by plants or trees (black walnut). They are *allelopathic*, that is compounds, which are toxic or growth stunting to many types of plants (it was long noticed that gardening under black walnut could be difficult or impossible). Lawsone, known as henna, was used since thousands of years, as a reddish plant dye to colour skin and hair, and juglone was used as a natural brown dye.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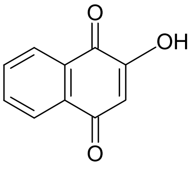
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[1] This paper was presented in part as poster at the 50th Anniversary Meeting "Challenges in Organic Chemistry", Eighth Tetrahedron Symposium, 26–29 June 2007, Berlin, Germany.

Correspondence: Roman E. Sioda, Department of Analytical Chemistry and Electrochemistry, Institute of Chemistry, University of Podlasie, ul. 3 Maja 54, 08-110 Siedlce, Poland.
E-mail: rsioda@tlen.pl

Results and discussion

There are several sources of mechanistic information coming from analyzing cyclic voltammetric curves, however, the most important one follows from the magnitude of the current intensity peak, I_p [A], and from the potential value of the peak, E_p [V]. The magnitude of the peak current intensity can be analyzed by means of the *Randles-Ševčik* Eq. (1):

$$I_\mathrm{p} = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} c, \qquad (1)$$

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], ν is the potential rate [V/s], and c is the concentration of substrate [mol/cm^3]. The equation can be rearranged so:

$$CF = (I_\mathrm{p}/Ac\nu^{1/2})^{2/3} = (4.18 \times 10^3) n D^{1/3} = k' \cdot n, \qquad (2)$$

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. (2) can serve to determine the number of electrons transferred in a given process, as has been shown earlier [2, 3]. An alternate method of calculation of n is proposed here, and consists of making a statistical regression analysis of I_p *vs.* $\nu^{1/2}$, and calculating n from the slope of the regression line, or calculating the expressions $I_\mathrm{p} \cdot \nu^{-1/2}$ for individual data points, taking a mean, and calculating n from the value of the mean:

$$(I_\mathrm{p} \cdot \nu^{-1/2})_\mathrm{mean} = \mathrm{m}^{-1} \sum I_\mathrm{p} \cdot \nu^{-1/2} \qquad (3)$$

and

$$n_\mathrm{mean} = 2.40 \times 10^{-4} \cdot D^{-1/3} [(I_\mathrm{p} \cdot \nu^{-1/2})_\mathrm{mean}/Ac]^{2/3}, \qquad (4)$$

where m is the number of experimental point pairs. Assuming that the diffusion coefficient for a group of analogous compounds has a similar value, and taking account of the fact that the significance of differences of individual D values is reduced by its cubic radical, Eq. (4) can be expressed using a constant term, k'':

$$n_\mathrm{mean} = k'' [(I_\mathrm{p} \cdot \nu^{-1/2})_\mathrm{mean}/Ac]^{2/3} \qquad (5)$$

The value of $k'' = 1/k'$ can be determined experimentally, if the value of n is known.

Table 1 Voltammetric peak's current intensity, $I_\mathrm{p}10^4/\mathrm{A}$, divided by square root of potential rate, $\nu/\mathrm{V\,s^{-1}}$, *vs.* potential rate. The compounds: naphthalene (*NA*); 1,3-dimethylnaphthalene (*1,3-DMN*); 2,6-dimethylnaphthalene (*2,6-DMN*); 1-naphthalenemethanol (*1-NM*), first and second peaks; 1-naphthalenaldehyde (*1-NA*); 1-naphthoic acid (*1-NCA*); 2-naphthoic acid (*2-NCA*). Peak potentials from Ref. [3]

No.	Potential rate, $\nu/\mathrm{V\,s^{-1}}$	$I_p10^4/A{*}\nu^{-1/2}/\mathrm{V}^{-1/2}\mathrm{s}^{1/2}$							
		NA	*1,3–DMN*	*2,6–DMN*	*1–NM*, 1st peak	*1–NM*, 2nd peak	*1–NA*	*1–NCA*	*2–NCA*
1	0.01	11.8	14.9	15.1	7.9	11.7	9.6	4.6	6.1
2	0.015	10.9	14.7	15.9	8.0	12.2	9.7	4.3	6.3
3	0.02	11.1	14.4	16.4	7.9	12.2	10.2	5.6	6.8
4	0.025	11.0	–	16.0	7.9	12.1	10.5	5.1	7.2
5	0.03	10.7	14.0	16.2	7.9	12.3	10.6	5.3	7.5
6	0.04	10.4	13.9	16.9	8.0	12.5	10.6	5.8	7.6
7	0.05	10.2	13.6	16.7	7.7	12.2	10.8	5.9	8.0
8	0.06	10.2	13.4	16.9	7.9	12.5	10.9	6.0	8.1
9	0.07	9.9	13.4	16.7	7.8	12.3	11.0	6.2	–
10	0.08	9.7	13.3	16.4	7.4	11.8	11.1	6.4	8.1
11	0.09	9.7	11.8	15.8	7.7	12.1	11.1	6.0	8.1
12	0.10	9.7	12.9	16.1	7.6	12.0	10.9	6.1	8.2
13	0.20	9.4	12.5	15.8	7.6	11.9	10.7	6.5	8.2
14	0.30	9.3	12.4	15.7	7.5	11.6	10.5	6.1	8.2
m	No. points	14	13	14	14	14	14	14	13
x	Mean	10.29	13.48	16.19	7.77	12.10	10.59	5.71	7.57
s	St. dev.	0.73	0.92	0.52	0.19	0.27	0.47	0.66	0.75

m Number of experimental points, *x* arithmetic mean, *s* standard deviation

Table 2 Voltammetric peak's current intensity, $I_p 10^4/\mathrm{A}$, divided by square root of potential rate, $\nu/\mathrm{V\,s^{-1}}$, *vs.* potential rate. The compounds: sodium salt of 2-naphthoic acid (*2-NCA*-Na), first and second peaks; 1-acetonaphthone (*1-AN*); 2-acetonaphthone (*2-AN*); 1,8-naphthalenedimethanol (*1,8-NDM*), first and second peaks; 1-naphthylacetate (*1-NAC*); benzoic acid (*BA*). Peak potentials from Ref. [3]

No.	Potential rate, $\nu/\mathrm{V\,s^{-1}}$	$I_p 10^4/A{*}\nu^{-1/2}/\mathrm{V^{-1/2}\,s^{1/2}}$							
		2-NCA-Na, 1st peak	*2-NCA*-Na, 2nd peak	*1-AN*	*2-AN*	*1,8-NDM*, 1st peak	*1,8-NDM*, 2nd peak	*1-NAC*	*BA*
1	0.01	1.3	3.7	11.8	12.7	10.7	12.5	10.1	6.5
2	0.015	1.4	3.3	11.6	12.5	10.7	12.5	10.0	6.5
3	0.02	1.9	4.9	11.6	12.2	10.4	12.3	10.0	6.6
4	0.025	2.0	5.2	11.2	11.3	10.5	12.5	9.7	6.9
5	0.03	2.2	5.4	11.0	11.8	10.4	12.4	9.5	6.9
6	0.04	2.0	5.9	11.2	11.8	10.2	12.2	9.4	7.2
7	0.05	2.2	5.6	11.1	11.7	10.1	12.2	9.2	7.0
8	0.06	2.1	6.0	10.8	11.4	10.0	12.2	9.1	7.3
9	0.07	2.5	6.4	10.5	11.5	9.8	12.0	8.9	7.0
10	0.08	2.4	6.7	10.6	10.5	9.2	12.1	8.7	6.8
11	0.09	2.4	6.5	10.6	11.2	9.6	12.0	8.8	6.8
12	0.10	2.7	7.0	10.4	10.6	9.8	12.0	8.8	6.7
13	0.20	2.7	7.4	–	10.0	9.2	11.6	8.7	6.6
14	0.30	2.8	7.4	9.7	9.8	8.9	11.4	8.3	6.8
m	No. points	14	14	13	14	14	14	14	14
x	Mean	2.19	5.81	10.93	11.36	9.96	12.14	9.22	6.83
s	St. dev.	0.45	1.25	0.58	0.88	0.58	0.33	0.57	0.24

m Number of experimental points, *x* arithmetic mean, *s* standard deviation

In Tables 1 and 2 are shown the experimental ($I_p \cdot \nu^{-1/2}$) parameters for a group of naphthalene derivatives, the calculated mean values, *x*, and standard deviations, s. From the mean values x, the mean number of electrons transferred per molecule of substrate, n_{mean}, were calculated, using the constant value $k' = 104.6$, as determined earlier [3]. The results of calculation are presented in Table 3.

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 [3]. 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. Earlier, it was shown that for a series of 26 naphthalene derivatives cyclic voltammetric oxidations, the experimental correlation was as follows [3]:

$$E_p[\mathrm{V}] = -0.531 \cdot E_{\mathrm{HOMO}}[\mathrm{eV}] - 2.985\,\mathrm{V} \qquad (6)$$

However, it was observed that the correlation [6] did not apply for 1-naphthol (**3**) 2-naphthol (**4**) [2], and **2**, the latter one containing also a hydroxyl group connected with the quinoid nucleus at the position 2. The measured values of E_p of these compounds are much less positive, than it follows from Eq. (6) (Fig. 1a and footnote of Table 3).[2] Thus, it is probable that the mechanism of the electron transfer changes [4]. As was shown earlier, for most of the naphthalene derivatives the prevailing mechanism consists of a formation of radical cations at the primary reaction step:

$$AH_2 - e^- = [AH_2]^{+\bullet}, \qquad (7)$$

$$[AH_2]^{+\bullet} + nH_2O = [(AH_2)\cdots nH_2O]^{+\bullet} \qquad (8)$$

where AH_2 is the substrate, and $[AH_2]^{+\bullet}$ is the radical cation, having an unpaired spin and a positive charge at the same time. The radical cation becomes hydrated, and the hydrate transforms into a charged activated complex shown in Eq. (8) [4].

As in the case of naphthols and lawsone, the oxidation starts at less positive potentials, it may mean that the oxidation goes more easily, and may be fa-

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[2] The presently measured potentials of the first oxidation peaks of naphthols are somewhat smaller, than the ones given earlier: $E_{p1} = 0.80\,\mathrm{V}$ for **3** and $E_{p1} = 0.94\,\mathrm{V}$ for **4** [2].

Table 3 Values of electrons transferred per molecule, n_{mean}, and 95% confidence limits, calculated according to Eq. (5), using data of Tables 1 and 2 and concentrations shown here. Experimental constant, $k'' = 9.57 \times 10^{-3}$. In last column n values calculated for constant potential rate, $\nu = 0.02\,\mathrm{V/s}$, from Ref. [3]

No.	Compound	Concentration, c/mM	Calculated number of electrons transferred/molecule, n_{mean}	No. of electrons transferred/ molecule, n, from Ref. [3]
1	Naphthalene	5.0	1.95 ± 0.05	1.8
2	1,3-Dimethylnaphthalene	5.0	2.35 ± 0.06	2.4
3	2,6-Dimethylnaphthalene	6.0	2.34 ± 0.03	2.1
4	1-Naphthalenemethanol	5.0	1.63 ± 0.02	1.6
			$2.19 \pm 0.02^{*}$	1.8*
5	1-Naphthaldehyde	5.0	1.99 ± 0.03	2.0
6	1-Naphthoic acid	5.0	1.32 ± 0.06	1.4
7	2-Naphthoic acid	5.0	1.59 ± 0.06	1.7
8	Sodium salt of 2-naphthoic acid	5.0	0.72 ± 0.05	–
			$1.35 \pm 0.11^{*}$	–
9	1-Acetonaphthone	5.0	2.03 ± 0.04	1.8
10	2-Acetonaphthone	5.0	2.08 ± 0.06	2.0
11	1,8-Naphthalenedimethanol	5.0	1.91 ± 0.04	2.0
			$2.18 \pm 0.02^{*}$	2.2*
12	1-Naphthylacetate	5.0	1.81 ± 0.02	1.8
13	Juglone (**1**)	9.0	1.18 ± 0.03	–
14	Lawsone (**2**)	8.0	0.82 ± 0.02	–
			$0.90 \pm 0.02^{*}$	–
15	1-Naphthol (**3**)	5.0	0.71 ± 0.01	–
			$1.50 \pm 0.06^{*}$	–
16	2-Naphthol (**4**)	5.0	0.75 ± 0.01	–
			$1.18 \pm 0.04^{*}$	–
17	Benzoic acid	5.0	1.48 ± 0.02	–

* Calculated values for the first and second peaks, respectively. Peak potentials from Ref. [3], except for **1** ($E_p = 1.90\,\mathrm{V}$), **2** ($E_{p1} = 1.26\,\mathrm{V}$ and $E_{p2} = 1.50\,\mathrm{V}$), **3** ($E_{p1} = 0.66\,\mathrm{V}$ and $E_{p2} = 1.65\,\mathrm{V}$), **4** ($E_{p1} = 0.90\,\mathrm{V}$ and $E_{p2} = 1.53\,\mathrm{V}$) and benzoic acid ($E_p = 2.02\,\mathrm{V}$)

cilitated by an assumed simultaneous hydroxyl proton transfer, *e.g.*:

$$AH(OH) \cdot H_2O - [e^- + H_3O^+] = AH(O^\bullet), \qquad (9)$$

$$AH(O^\bullet) \rightarrow \text{polymerization} \qquad (10)$$

i.e., there is a "concerted" electron and hydroxonium ion (proton) transfer with the formation of a naphthoxyl radical (**5**), which immediately polymerizes. It is believed that water molecules participate in the process by solvating naphthols and lawsone, *i.e.*, through hydrogen bond formation with the hydroxyl, and, thus, facilitating the hydroxonium ion abstraction on the electro-oxidation. An analogous, but reversed, *i.e.*, for electron and proton addition, "concerted" mechanism was proposed for the electro-reduction of benzaldehyde (**6**) by cyclic voltammetry [5].

It is interesting that juglone, which is a compound with a hydroxyl group at the position 5 of 1,4-naphthoquinone structure of **1**, shows a value of $E_p = 1.90\,\mathrm{V}$ in a fairly acceptable agreement with an hypothetical value from the experimental correlation of Eq. (6), *i.e.*, 2.13 V ($E_{\mathrm{HOMO}} = -9.626\,\mathrm{eV}$, Ref. [3]). In this case, it is probable that a strong *intramolecular* hydrogen bond forms between the hydroxyl proton and the neighboring oxygen of the carbonyl group of the naphthoquinone structure. As a consequence, the hydroxyl proton of **1** is less sensitive to the type of the "concerted" mechanism expressed by Eq. (9). By performing molecular orbital calculations, it is possible to show that the average distance between the hydroxyl proton and neighboring carbonyl oxygen is only 1.97 Å, as compared with the distance of 0.97 Å in the hydroxyl group itself. The calculated energy of the hydrogen bond in **1** is $22.2\,\mathrm{kJ\,mol^{-1}}$, while for **2** it is $9.8\,\mathrm{kJ\,mol^{-1}}$ for a distance of 2.23 Å between the hydroxyl proton and the carbonyl oxygen in position 1 and 0.97 Å for OH bond. Thus, it seems that the internal hydrogen bond in lawsone is substantially strong than in juglone, and allows the "concerted" mechanism according to Eq. (9). The calculation was performed using the AM1 program

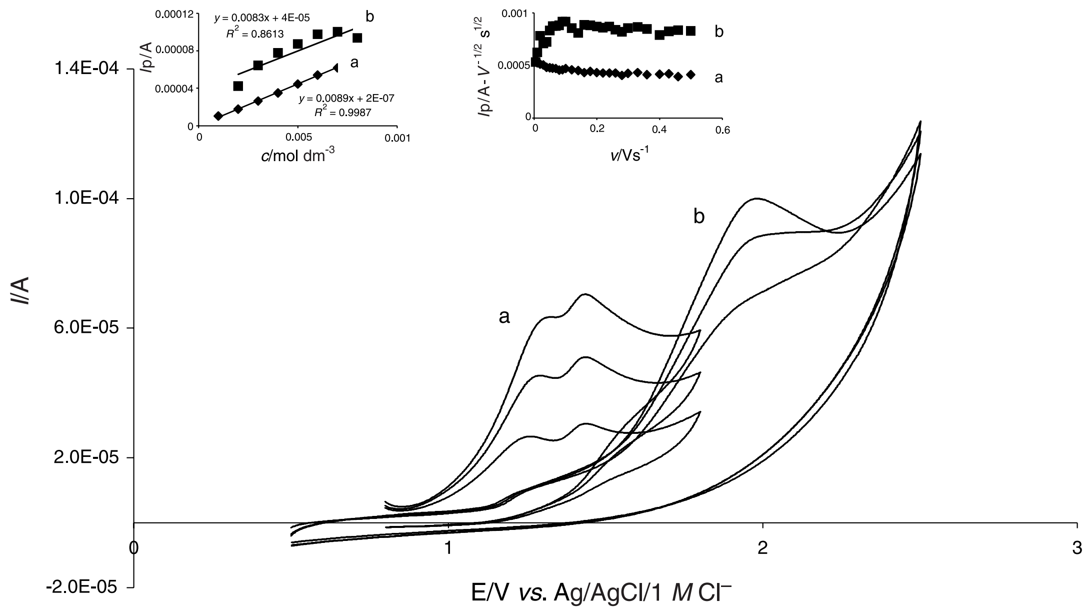

Fig. 1 Cyclic voltammetric curves of: (a) lawsone (**1**) and (b) juglone (**2**). Respective concentrations, in order of increasing curves' heights: 3.0, 5.0 and 7.0 mm: potential rate 0.02 V/s. Inserts: on left – peak current intensity *vs.* substrate concentration, on right – peak current intensity divided by square root of potential rate *vs.* potential rate; data for lawsone (a) correspond to peak at $E_{p1} = 1.26$ V, and for juglone (b) to one at $E_p = 1.90$ V; concentrations are in Table 3

of WinMOPAC *2.0* [6].[3] Figure 1 shows the cyclic voltammetric curves of **2** and **1**.

By application of Eq. (5) it can be shown that for most of the naphthalene derivatives measured, the average number of electrons transferred is 2, meaning that possibly a hydroxyl group is introduced into the aromatic nucleus [3]:

$$AH_2 + 3H_2O - 2e^- = AH(OH) + 2H_3O^+ \qquad (11)$$

On the other hand, in the case of naphthols, lawsone and juglone, on average one electron or even less are transferred, possibly indicating the "concerted" electron and proton transfer according to Eq. (9), followed by a fast polymerization reaction of the resulting naphthoxyl or naphthoquinoxyl (**7**) radicals. Such a follow-up polymerization mechanism is strongly indicated by the shape of the voltammetric oxidation peaks, which are broad, and shift to higher potentials with the increase of concentration of substrates. The electrons transferred per molecule calculated in this paper basically agree in values with the ones evaluated earlier [3], also shown in Table 3. It indicates that the two types of calculation of the number of electrons transferred, using the *Randles-Ševčik* equation, one depending on the measurements of a peak current intensity *vs.* concentration of substrate, and the other on the peak current intensity *vs.* potential rate, give basically equivalent results. The fuller elucidation of details of the electro-oxidative reaction requires conducting preparative electrolyses, starting in the scale of a few tenths of milligram of the substrate [7].

Experimental

Similarly as in the earlier papers cited, the cyclic voltammetry was performed using an Auto-Lab PGST 12 instrument (Eco-Cell, Holland). A glassy carbon disk electrode (Metrohm) of 3 mm diameter and geometric surface area $A = 0.07069$ cm^2 was used as the working electrode. The electrode was polished with Al_2O_3 powder of 0.05–0.1 μm grain size before each

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[3] These calculations were confirmed by *PM*3 method, which gave hydrogen bonding energies: 29.1 kJ mol^{-1} for **1** and 6.5 kJ mol^{-1} for **2**. *Ab initio* methods: *B*88-*LYP* DZVP and *B*3*LYP*/6-31 + *G*(*d*,*p*) gave, respectively, 55.3 and 52.8 kJ mol^{-1} for **1**, and 31.6 and 29.4 kJ mol^{-1} for **2**. The latter *ab initio* method gave the following distances: OH bond 0.9914 Å, O···H bond 1.7077 Å for **1**, and OH bond 0.9794 Å, O···H bond 2.0306 Å for **2**. In the case of **1**, hydrogen bonding was also evident from the calculated, by the latter *ab initio* method, stretching frequency of OH of 3326.9 cm^{-1}, while a similar calculation gave OH stretching frequency of 3615.8 cm^{-1} for **2**. Calculated OH stretching frequencies for "open structures", *i.e.*, OH bonds turned 180°, gave 3805.4 cm^{-1} for **1** and 3801.4 cm^{-1} for **2**. No crystallographic data were found in literature.

determination. The potentials were measured *vs.* 1.0 *M* KCl Ag/AgCl electrode. A mixed solvent, acetone and water (1:1, ν/ν), was applied to obtain sufficiently high solubility of substrates and electric conductivity with added 0.1 *M* $(CH_3)_4N(BF_4)$ supporting electrolyte. The measurements were performed at room temperature of around 22°C. The chemicals studied were used as purchased from *Aldrich*, *Fluka*, and *Merck*. Their specified purity, from >95.0 up to 99.0%, was confirmed by GC-MS analyses using Hewlett-Packard and Shimadzu instruments.

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