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Electrochemical oxidation of 2-methylnaphthalene-1,4-diacetate

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Cyclic-voltammetric measurements show that 2-methylnaphthalene-1,4-diacetate is electrochemically oxidized on glassy-carbon electrode in glacial acetic acid at +1.45 V vs SCE. The process is irreversible and diffusion controlled. Preparative controlled-potential electrolysis indicates that 2-methyl-1,4-naphthoquinone is a sole product. The material and current yields of the process are 94 and 99%, respectively.

Keywords: *electrochemical oxidation*, *2-methylnaphthalene*, *2-methyl-1,4-naphthoquinone*, *vitamin K*, *2-methylnaphthalene-1,4-diacetate*

1. Introduction

The oxidation of 2-methylnaphthalene (MN) to 2-methyl-1,4-naphthoquinone (MNQ) is a challenging problem in catalysis research. This reaction is the key step in the synthesis of vitamin K and its derivatives, which serve as blood coagulating factors [1] and as a supplement in animal feed [2]. The preparation of naphthaquinones usually requires the direct oxidation of arenes by stoichiometric quantities of chromic acid/sulfuric acid [3, 4]. The reaction can be also achieved by the use of Ce(IV) compounds as oxidants [5]. Recently, some new catalytic methods of MNQ preparation by hydrogen peroxide oxidation of MN catalysed by Pd (II)-polistyrene sulfonic acid resin [6] and methyltrioxorhenium (CH_3ReO_3) [7] have been reported. The process can also be performed by the use of potassium monopersulfate ($KHSO_5$) as an oxidant, which is catalysed by water-soluble metalloporphirynes [8]. Dioxygen in the presence of vanadomolybdenophosphoric heteropolyacids or their salts in a two-phase system (water and an organic solvent) was also used [9, 10]. The yield of the product and the selectivity, however, are still not perfect. The indirect electrolysis with ruthenium compounds and dichromate as mediators were also applied in the process [11–13]. In previous work [14] we reported that the electrochemical oxidation of MN in glacial acetic acid gives monoacetates, mainly 2-methylnaphthalene-1-acetate. 2-methylnaphthalene-1,4-diacetate (MNDA) and MNQ were also formed. The results were similar to those reported elsewhere [15, 16]. Further investigations have shown that about 10% of MN is transformed to equimolar quantities of MNDA and MNQ. Taking into account the observation [17] that hydroquinone diesters are resistant to oxidation, the question has raised if MNQ is formed independently or via MNDA. It was found, however, that diacetyl and dimethyl esters of durohydroquinone undergo anodic oxidation to give quantitative amounts of duroquinone [18] and that the electrochemical oxidation of diphosphate ester of 2-methylnaphthahydroquinone yields the corresponding quinone [19]. Those facts prompted us to investigate the electrochemical behavior of MNDA.

2. Experimental details

2.1. *Apparatus*

Cyclic voltammetry was performed with a Bioanalytical Systems Model CV-50W cyclovoltammetric analyser. These measurements were made with a 10 mL microcell assembly that was adopted for the working electrode (a Bioanalytical Systems glassy-carbon electrode of area 0.09 cm^2), a platinum sheet (area 7 cm^2) auxiliary electrode, and a Ag/AgCl reference electrode filled with aqueous tetramethylaminium chloride solution and adjusted to 0.00 V vs SCE [20] with a solution junction via a Pyrex glass tube closed with crocked soft-glass beds that was contained in a Luggin capillary. The cyclic voltammograms were initiated at the rest potential of the solution and voltages are reported against the SCE. Controlled-potential preparative electrolysis was performed in an H-cell divided with a medium porosity glass frit. The cell was equipped with a glassy carbon plate (40 mm × 20 mm × 5 mm) working electrode, a platinum sheet (area 30 cm^2) auxiliary electrode, and the above described Ag/AgCl reference electrode. The electrolyses were accomplished with a three-electrode potentiostat (Princeton Applied Research model 273) and a TZ 21S recorder (Laboratorni Pristroje). The charge was calculated by numerical integration of current–time relationship.

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2.2. *Chemicals and reagents*

Unless stated otherwise, the reagents for investigations and synthesis were the highest purity commercially available and were used without further purification. MNDA was prepared from 2-methyl-1,4-naphthoquinone (Fluka) by reductive acetylation [21]. The product was crystallized several times from 60% ethanol until the melting point of the solid was 116 °C. Anhydrous lithium perchlorate (ICN Chemicals) was dried in vacuum to a constant weight at 120 °C [22]. Glacial acetic acid (POCH) was purified by the procedure described elsewhere [22], except that the water content was not determined by the Karl–Fisher method, but the frozen acid was partially frozen out [15] and the fraction of melting point 16.6 °C was used.

2.3. *Methods*

Cyclic voltammetric measurements of MNDA were registered for different substrate concentrations (1×10^{-4}–2×10^{-3} M) and different scan rates (0.005–0.25 V s^{-1}), whereas, in the case of MNQ, only one value of scan rate equal to 0.1 V s^{-1} but the same set of the substrate concentrations was chosen. A 1 M solution of $LiClO_4$ in glacial acetic acid was always used as the supporting electrolyte.

During controlled-potential preparative electrolysis both compartments of the H-cell were filled with 50 cm^3 of 1 M $LiClO_4$ in glacial acetic acid, and the potential of the anode was set to +1.56 V (vs SCE). The solution in the anodic compartment was constantly stirred. After a residual current (about 1 mA) was reached, 0.77 mmol (15.4 mM) of MNDA was added to the solution. In the course of the electrolysis the samples (0.5 cm^3) were withdrawn from the anolyte and were used for the concentration determination of the substrate (MNDA) and the desired product (MNQ). These analyses were performed by means of cyclic voltammetry. When the total charge had reached 100 C the electrolysis was stopped.

Thin layer chromatography (TLC) was performed on silicagel plates (Kiessegel 60 F254, Merck). The solvent consisted of 40 vol % ethyl acetate and 60 vol % carbon tetrachloride. The spots of the substrate and products were visualized either by UV-light or after the mixture of concentrated H_2SO_4 with 1% of formalin was sprayed on the plate surface [23]. All measurements were performed at 298 ± 1 K. The results presented are the means of five measurements. The error in the potential measurements did not exceed ±0.005 V.

3. Results and discussion

The cyclic voltammogram of MNDA is presented in Fig. 1. In the first anodic scan a peak (A) at +1.45 V vs SCE (scan rate 0.1 V s^{-1}) is observed. The peak potential depends linearly on the scan rate. The dependence of the peak potential on logarithm of scan rates is linear with a slope 0.066 (Fig. 2). The height of the peak (at a constant scan rate) depends linearly on the substrate concentrations. In the reverse cathodic scan, a peak (B) at +0.1 V (scan rate 0.1 V s^{-1}) is observed. The peak height increases with increase in substrate concentration and the number of scans performed. With increase in scan rate the peak potential is shifted negatively. In the second anodic scan the height of the previously described peak (A), decreases and a new peak (C) at +0.27 V (scan rate 0.1 V s^{-1}) appears. The slope of the E_p^A vs log v dependence (0.066) indicates that the oxidation of MNDA is an irreversible electrochemical process. Table 1 presents the values of βn_β calculated for different scan rates by the methods described by

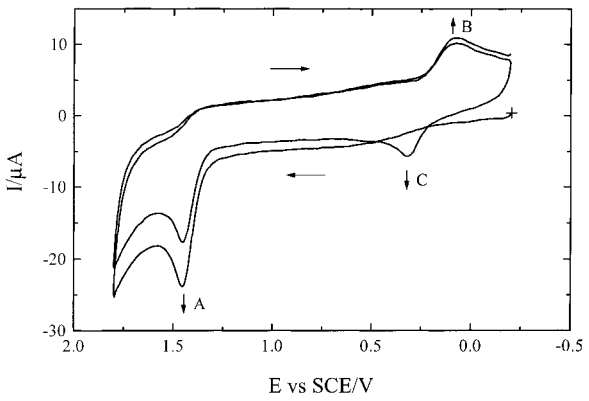


Fig. 1. Cyclic voltammogram of 1 mM 2-methylnaphthalene-1,4-diacetate (MNDA) in glacial acetic acid. Scan rate 0.1 V s^{-1}; glassy carbon working electrode (0.09 cm^2).

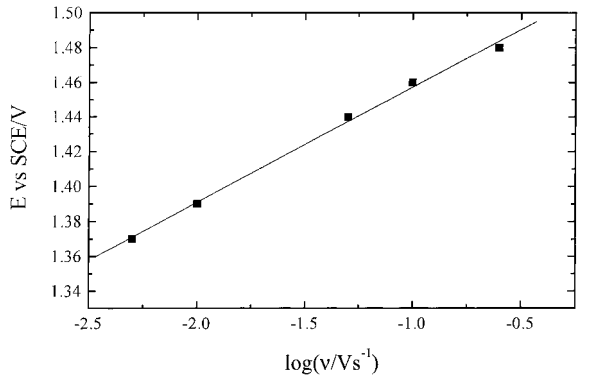


Fig. 2. The dependence of the peak potential (E_p) against the logarithm of scan rate (log v) for the irreversible reduction of 2-methylnaphthalene-1,4-diacetate (MNDA) in glacial acetic acid.

Table 1. Parameters of the electrochemical oxidation of 2-naphthalene-1,4-diacetate on glassy carbon electrode in glacial acetic acid

Scan rate /V s^{-1}	*Peak potential* /V	βn_β
0.005	1.375	0.48
0.01	1.393	0.47
0.05	1.440	0.49
0.1	1.461	0.48
0.25	1.480	0.47

Matsude and Ayabe [24]. The mean value of βn_β is 0.48.

The heights of the peaks B and C increase when MNQ is added to the solution of MNDA in glacial acetic acid. This indicates that peak B corresponds to the reduction of MNQ, whereas peak C is caused by the oxidation of 2-methyl-1,4-dihydroxynaphthalene. For comparison, Fig. 3 presents the cyclic voltammogram of MNQ. The positions of the B and C peaks indicate that the reduction of MNQ is a quasi-irreversible process. The difference between the peak potentials increases with increase in scan rate. This observation is in agreement with already reported [25]. The quasi-reversible quinone/hydroquinone system on carbon paste electrode was previously observed [26] and our current research also indicates that the same phenomenon on glassy carbon electrode in anhydrous acetonitrile takes place. These results suggest the mechanism of electrochemical oxidation of MNDA presented in Scheme 1.

The preparative potential-controlled electrolyses confirm the proposed mechanism. After the passage of 100 C of charge, the anolyte was diluted with water tenfold and the organic components were extracted with diethyl ether. The components of the extracted mixture were separated and identified by TLC. Except for unreacted substrate only MNQ was present. Authentic samples were used to confirm product identification. To identify acetic anhydride, which is a byproduct of the reaction, 1.8 mmol of *m*-nitroaniline was introduced into the anolyte after the electrolysis. After 24 h the solution was diluted with water, the extraction with ethyl acetate was performed, and TLC analysis of the extract was carried out. Only *m*-nitroacetanilide was detected. It is known [27] that the acylation of *m*-nitroaniline or 2,4-dichloroaniline can be performed only by the use of acetic anhydride and not by acetic acid as in the case of aniline.

The plot of the amount of MNQ formed during electrolysis and the amount of MNDA used is linear with a slope of 0.94 (Fig. 4(a)). Similarly, the plot of

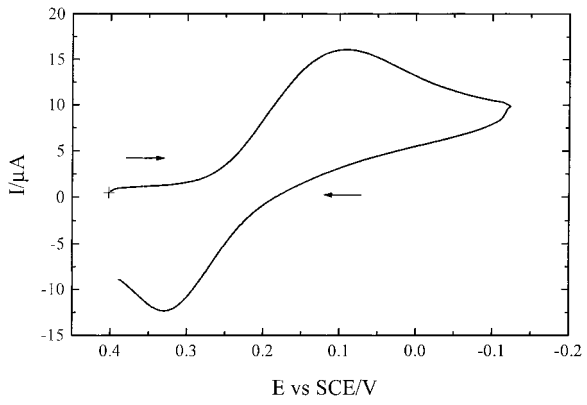
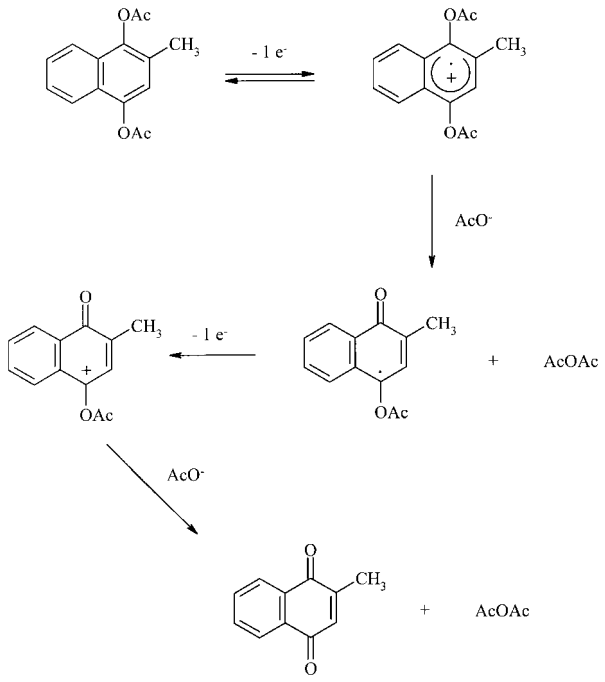


Fig. 3. Cyclic voltammogram of 0.5 mM 2-methylnaphthaquinone (MNQ) in glacial acetic acid. Scan rate 0.1 V s^{-1}; glassy carbon working electrode (0.09 cm^2).



Scheme 1 The proposed mechanism.

the amount of charge required for the formation of detected amount of MNQ versus the real charge used in electrolysis is also linear with a slope of 0.99 (Fig. 4(b)). These factors indicate that the material and current yields are 94 and 99%, respectively.

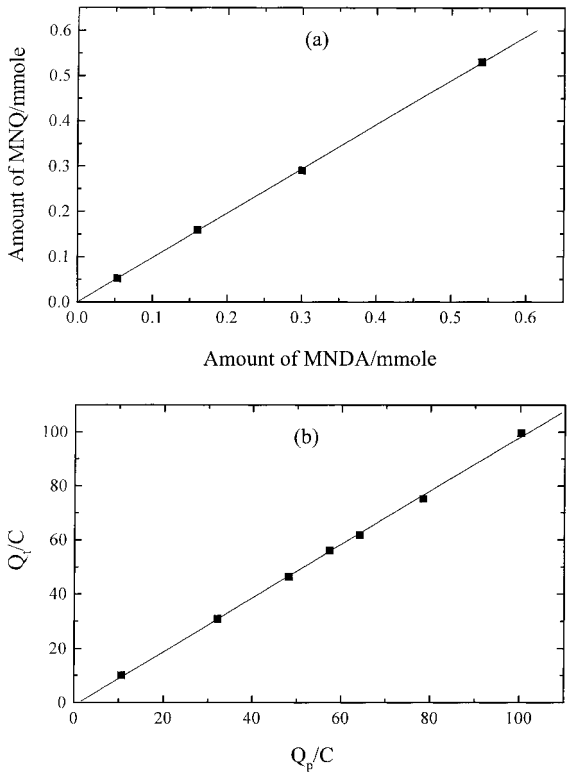


Fig. 4. The dependence between: (a) the amount of 2-methylnaphthaquinone (MNQ) formed during the electrolysis and the amount of 2-methylnaphthalene-1,4-diacetate (MNDA) used in the reaction; (b) the amount of charge required for the formation of a detected amount of MNQ (Q_t) and the real charge consumed in electrolysis process (Q_p).

4. Conclusion

It is shown that the electrochemical oxidation of 2-methylnaphthalene-1,4-diacetate in glacial acetic acid, yields 2-methyl-1,4-naphthoquinone as a sole product. The process can be considered as an alternative step in a route for vitamin K preparation.

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