Electrochemical oxidation of 1-phenyl-4-methyl-pyrazolidone on boron-doped diamond and platinum electrodes

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The electrochemical oxidation of 1-phenyl-4-methyl-pyrazolidone (PMP) on a boron-doped diamond electrode has been studied and compared with the oxidation on a platinum electrode. The presence of PMP in 0.1 M NaOH solution determines the increase of oxygen evolution potential on both BDD diamond and platinum anodes, possibly because of the adsorption of PMP or its oxidation intermediates. Accomplishment of an electric charge adequate to the PMP amount during the electrolysis of PMP alkaline solution in the potential region of electrolyte decomposition results in the oxidation of about 94% PMP on the BDD anode, presumably via electrogenerated hydroxyl radicals, and only ~33% on the Pt anode. The results showed that the platinum anode was completely deactivated during electrolysis in alkaline PMP solution.

Key words: boron-doped diamond electrode, electrochemical oxidation, 1-phenyl-4-methyl-pyrazolidone

INTRODUCTION

The wide potential window for water discharge on a boron-doped diamond (BDD) electrode makes it highly usable for an effective electrooxidation of various toxic organic compounds in wastewater. BDD has an inert character with weak adsorption properties and serves in the oxidation process as an inactive anode. Numerous investigations with BDD electrodes made by Comninelis and co-workers [1–6], summarized in a review [7], proposed that both the oxidation of organic compounds and oxygen evolution proceed on BDD via intermediates of hydroxyl radicals produced at the anode:

$$BDD + H_2O \rightarrow BDD(OH^\cdot) + H^+ + e^-, \qquad (1)$$

$$BDD(OH^\cdot) + R \rightarrow BDD + mCO_2 + nH_2O + H^+ + e^-. \qquad (2)$$
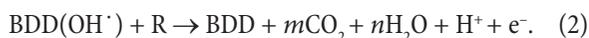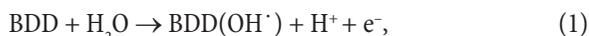
Reaction (2) competes with the reaction of hydroxyl radical discharge to O_2:

$$BDD(OH^\cdot) \rightarrow BDD + 1/2O_2 + H^+ + e. \qquad (3)$$
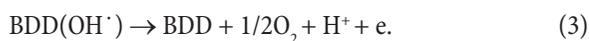
R denotes an organic compound containing no heteroatom, which is fully oxidized according to the schematic reaction equation (2) (m and n values depend on the composition of R). Simultanuously, there proceeds a competetive side-reaction (3) of O_2 evolution without participation of anode surface. The possibility to oxidize formic, oxalic, benzoic, salicylic acids [3, 4, 8], phenols [5], chlorophenols [2, 6, 9, 10], triazines [11] and some other organic compounds has been shown using BDD. The oxidation can proceed by direct electron transfer in the potential region of water stability or in an indirect way via electrogenerated hydroxyl radicals or other oxidizing agents generated on the surface of the anode at water decomposition potentials.

Oxidation of aromatic and heterocyclic compounds in the potential region of water stability by direct electron transfer often leads to the deactivation of electrode surface due to the deposition of anodically generated polymeric adhesive products. Deactivation can be inhibited in the potential region of electrolyte decomposition when oxidation proceeds via electrogenerated hydroxyl radicals.

Advantages in the application of BDD electrodes stimulated the present work in which anodic oxidation of the aromatic compound 1-phenyl-4-methyl-pyrazolidone (PMP, $C_{10}H_{12}ON_2$), using a BDD electrode, was investigated and

compared with the oxidation on a platinum electrode. This compound is a constituent of spent photographic developers and partially determines the noxiousness of phototreatment wastewaters.

EXPERIMENTAL

The BDD electrode (size 12×12 mm) was purchased from the Swiss Center for electronics and microtechnology SA Neuchatel-Switzerland. Its specification: substrate – monocrystalline silicon, resistivity 10–20 MOhm cm, BDD coating 1.2 µm thick, 1 000 ppm boron, backside Ti–Au metallization (approx. 1 µm thick).

Electrochemical measurements were performed with a PI-50 1.1 potentiostat (Russia), using a cell schematically depicted in Fig. 1. A Luggin capillary was inserted in the cell when anode polarization was measured. The working electrode was a BDD or Pt plate of 0.8 cm² geometric area, the reference electrode was Ag/AgCl, and the counterelectrode was a platinum plate. Anode potentials in the voltammograms are presented in the Ag/AgCl reference electrode scale. The bulk electrolysis of PMP solution was carried out in the same cell using a BDD or Pt anode and a Pt cathode. Electrolyte stirring was implemented by turning a glass bar inserted in the cell. The volume of solutions used in the electrochemical experiments was 15 ml. Experiments were carried out at an ambient temperature.
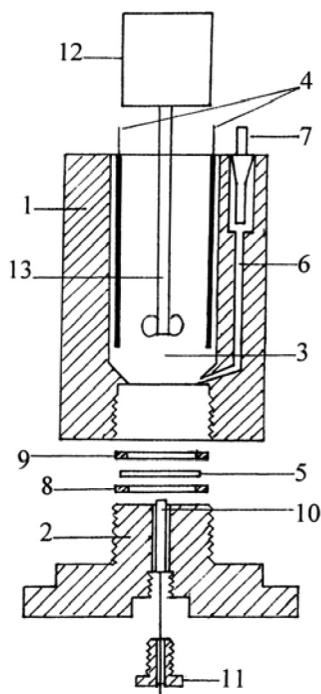
Chemical oxygen demand (COD) of the test solutions was established by the standard potassium dichromate oxidation method, using a Spectroquant TR 320 reactor and a Spectroquant Picco Colorimeter.

Organic compounds present in the solutions were analyzed by the gas chromatography method (GC/MS). Diethyl ether was used as an extrahent for the recovery of organic compounds. Before extraction, the solution pH was adjusted to 2.0. The GC/MS analysis was carried out on an HP 5 890 (Hewlett Packard) gas chromatograph with an HP 5971 mass selective detector and an HP 7 673 split / splitless injector. The separation was performed on a CP-Sil 8 CB silicon capillary column (50 m × 0.32 mm, film thickness 0.25 µm). The GC oven temperature was programmed as follows: from 60 °C it was increased to 250 °C at the rate of 20 °C/min, and the final temperature was kept for 5 min. The temperature of the injector and the detector was 250 °C. The flow rate or the carrier gas (helium) was 1 ml/min. Mass spectra in electron mode were generated at 70 eV.

Analytical grade PMP, H_2SO_4 and NaOH reagents were supplied by the "Reachim" company and used as received.

RESULTS AND DISCUSSION

Polarization measurements on both BDD and Pt electrodes showed that the oxygen anodic evolution potential increased with the PMP concentration (Figs. 2 and 3), possibly because of PMP adsorption on the anode.

One of the problems in the anodic oxidation of organic compounds, as mentioned above is connected with electrode fouling by oxidation products, resulting in a partial or complete electrode deactivation. Consecutive cyclic polarization curves revealed a practically complete Pt anode deactivation in an alkaline solution containing PMP (Fig. 4), while the same solution deactivated the BDD electrode only partially
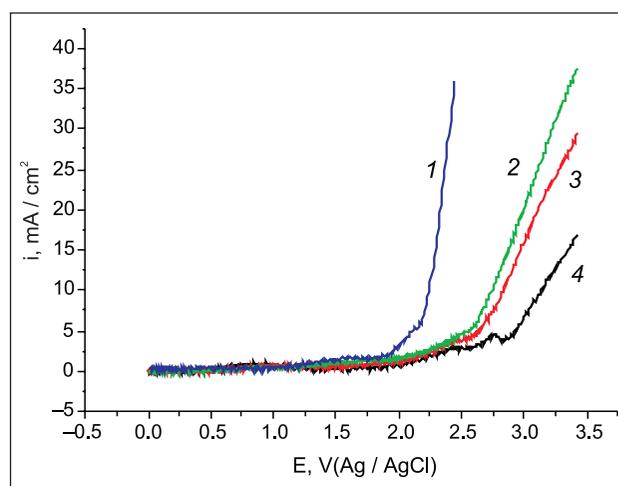

Fig. 1. Scheme of the cell for voltammetric measurements and bulk electrolysis. *1* – cell body, *2* – bottom cover, *3* – investigative solution, *4* – cathode, *5* – anode, *6* – Luggin capillary, *7* – reference electrode, *8* – ringed teflon gasket, *9* – siliconic sealant, *10* – anode contact, *11* – pressing screw, *12* – motor, *13* – glass stirrer

Fig. 2. Voltammetric i–E curves obtained on BDD anode in 0.1 M NaOH solution (*1*) and with the addition of PMP (mmol/l): *2* – 5, *3* – 8, *4* – 14. Scan rate 20 mV/s
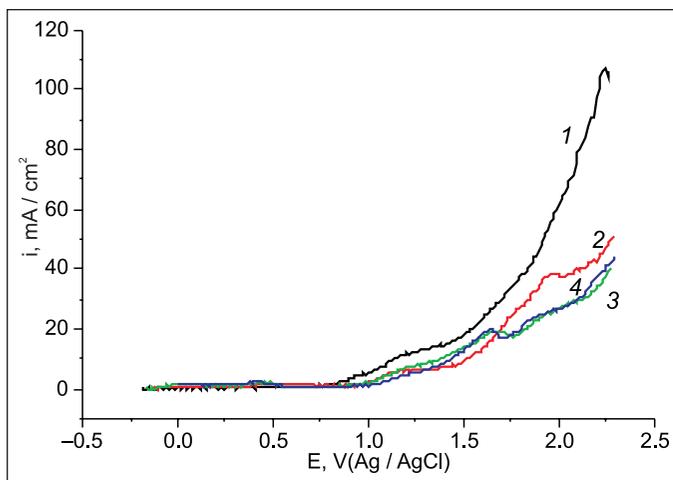
Fig. 3. Voltammetric i–E curves obtained on Pt electrode in 0.1 M NaOH solution (*1*) and with the addition of PMP (mmol/l): *2* – 5, *3* – 8, *4* – 14. Scan rate 20 mV/s
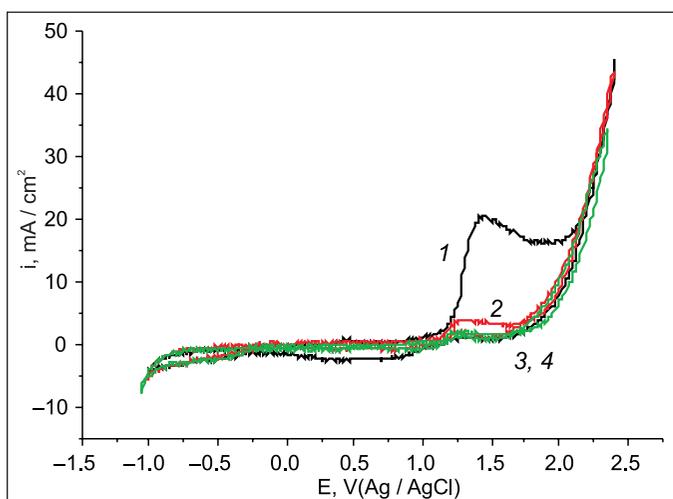

Fig. 4. Consecutive cyclic (*1–4*) voltammograms for Pt electrode in 0.1 M NaOH + 20 mmol/l PMP solution. Scan rate 50 mV/s
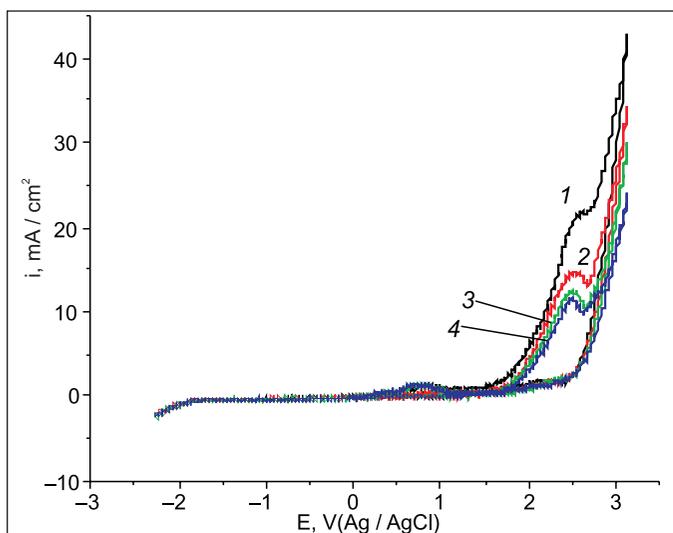

Fig. 5. Consecutive cyclic (*1–4*) voltammograms for BDD electrode in 0.1 M NaOH + 20 mmol/l PMP solution. Scan rate 50 mV/s

(Fig. 5). Apparently, PMP or its oxidation products were adsorbed on the BDD electrode more weakly. Another reason for Pt deactivation may be the increased rate of OH˙ radical transformation into O_2 molecules, which are worse oxidizing agents than OH˙.

Some galvanostatic tests were carried out to check the change in COD and solution components. Constant 10 mA current was passed through the cell (Fig. 1) containing PMP solution. COD changes during electrolysis are shown in Tables 1 and 2.

Theoretical COD values were calculated on the ground of the PMP oxidation reaction:

$$2C_{10}H_{12}ON_2 + 27O_2 \rightarrow 20CO_2 + 4NO + 12H_2O. \quad (4)$$

According to reaction (4), one g-mol of PMP reacts with 13.5 g-mol of oxygen, so the full oxidation of 5 mmol PMP requires 2 160 mgO_2. This value is in line with that determined for 5 mmol/l PMP solution in our work (2 150–2 200 mgO_2/l).

The theoretical COD rest value (COD_T) means the rest of COD after passing a certain amount of electric charge assuming its full-scale consumption for PMP oxidation and was calculated by the formula: COD_T = COD_I – Q · 8 · 1 000/26.8 (mgO_2/l), where COD_I is the initial COD mgO_2/l, Q is current charge, Ah/l. 8 is the equivalent mass of oxygen g/eq, 26.8 is Ah/eq.

It should be noted that PMP solution in 1 M H_2SO_4 is not stable: yellow sediments, possibly precipitates of polymeric compounds, are formed in the course of time, determining COD decrease. Therefore, in the initial stage of electrolysis, the COD value was less than the theoretical one (Table 1). Further experiments were performed in more stable alkaline solutions. Data presented in Table 2 show that PMP oxidation in 0.1 M NaOH solution did not correspond to the electric charge passed through the cell. It might be caused by mass-transfer limitations; besides, part of the current could be consumed for the discharge of oxygen which did not react with PMP.

As data of Table 2 show, COD decrease in NaOH solution is less than theoretical, partially because of mass-transfer limitation, while the stirring does accelerate PMP destruction, especially at the final stage

Table 1. **Dependence of chemical oxygen demand (COD) on the electric charge passed through 1 M H_2SO_4 + 5 mmol/l PMP solution. BDD anode. Initial COD_I = 2 150 mgO_2/l. I = 10 mA**

Q, Ah/l	COD, mgO_2/l	Theoretical COD_T rest value, mgO_2/l
1	1 650	1 851
2	1 420	1 553
3	1 305	1 254
4	1 080	956

Table 2. **COD dependence on the electric charge passed through 0.1 M NaOH + 5 mmol/l PMP solution. BDD anode. Initial COD_i = 2 200 mgO_2/l. I = 10 mA**

Q, Ah/l	COD, mgO_2/l		Theoretical COD_T rest value, mgO_2/l	Instantaneous current efficiency (ICE)*,%	
	without stirring	with stirring		without stirring	with stirring
1	2 050	2 045	1 901	50	52
2.4	1 870	1 875	1 484	46	45
4.8	1 575	900	767	44	90
7.4	370	140	0	83	93

* ICE(%) = (COD_i–COD / COD_i–COD_T) × 100.

Table 3. **COD dependence on the electric charge passed through 0.1 M NaOH + 5 mmol/l PMP solution. Pt anode. Initial COD_i = 2 200 mgO_2/l. I = 10 mA**

Q, Ah/l	COD, mgO_2/l		Theoretical COD_T rest value, mgO_2/l	Instantaneous current efficiency (ICE), %	
	without stirring	with stirring		without stirring	with stirring
1	2 100	2 000	1 901	33	67
2.4	1 920	1 900	1 484	39	42
4.8	1 440	1 450	767	53	52
7.4	1 450	1 400	0	34	36

of electrolysis. The considerable increase of instantaneous current efficiency at the end of electrolysis may be due to the depuration of the anode.

Anodic PMP oxidation on the Pt electrode proceeds until approximately 33% of organics is decomposed, and then its oxidation ceases (Table 3). Stirring enhanced the oxidation process at the initial stage of electrolysis.

These data confirm the presumption about Pt electrode deactivation by polarization measurement in the alkaline solution. The GC/MS analysis shows (Fig. 6a) that alongside PMP (retention time t_R = 11.7), phenol (~1%, t_R = 5.8) and an unidentified organic compound of a high molecular mass (~7%, t_R = 14.4) were present in the initial solution.

PMP can oxidize with formation of a free radical, which disproportionates forming 1-phenyl-4-methyl-3-pyrazolidone (I) and 1-phenyl-4-methyl-3- hydroxypyrazole (II) [12]:
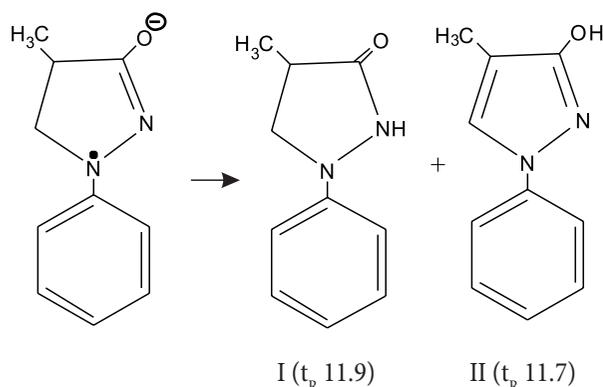
I (t_R 11.9)   II (t_R 11.7)

The second peak in Fig. 6 (t_R = 11.7) corresponds mainly to 1-phenyl-4-methyl-3-hydroxypyrazole (II) and a negligible part of it to 1-phenyl-4-methyl-3-pyrazolidone (I) (t_R = 11.9). These compounds were identified by mass spectrometric fragmentation.

After 4.8 Ah/l electrolysis of 0.1M NaOH + 5 mmol/l PMP solution with a BDD electrode, remain 1–5% of PMP (Fig. 6b) and after 7.4 Ah/l electrolysis only 0.3–0.8% of PMP remain in the solution (Fig. 6c). The rest of organics, which determines the remaining COD, consists of some unidentified compounds. Evidently, a small amount of PMP decomposes only partially. The rest of organics determines 140 mgO_2/l COD, thus about 94% of PMP is fully oxidized. Meanwhile, after passing 4.8 and 7.4 Ah/l electric charges using a Pt anode, in the solution there remain ~75 and 77% of PMP, respectively (Fig. 6d, e). Evidently, the Pt anode at a certain time is fully blocked for PMP oxidation.

So, data of anodic polarization, COD and GC/MS measurements are well related and show that PMP anodic oxidation proceeds on the BDD electrode more effectively than on the Pt electrode.

The fact that in the case of the partial deactivation of BDD the electrooxidation of PMP proceeds with a sufficient effectiveness suggests that BDD acts as an outher-sphere inactive electrode on which oxidation reaction occurs without adsorption of the reagent, via electrogenerated hydroxyl radicals. In contrast, for the oxidation on the Pt electrode, PMP adsorption is required, and in the case of electrode fouling the oxidation discontinues. Pt deactivation could be determined also by the increased rate of OH˙ transformation in the weaker oxidant O_2.

CONCLUSIONS

The presence of PMP in 0.1M NaOH solution determines the increase of the oxygen evolution potential on both BDD diamond and platinum anodes, presumably because of the adsorption of PMP or its oxidation intermediates. Accomplishment of electric charge adequate to the PMP amount during electrolysis of PMP alkaline solution in the potential region
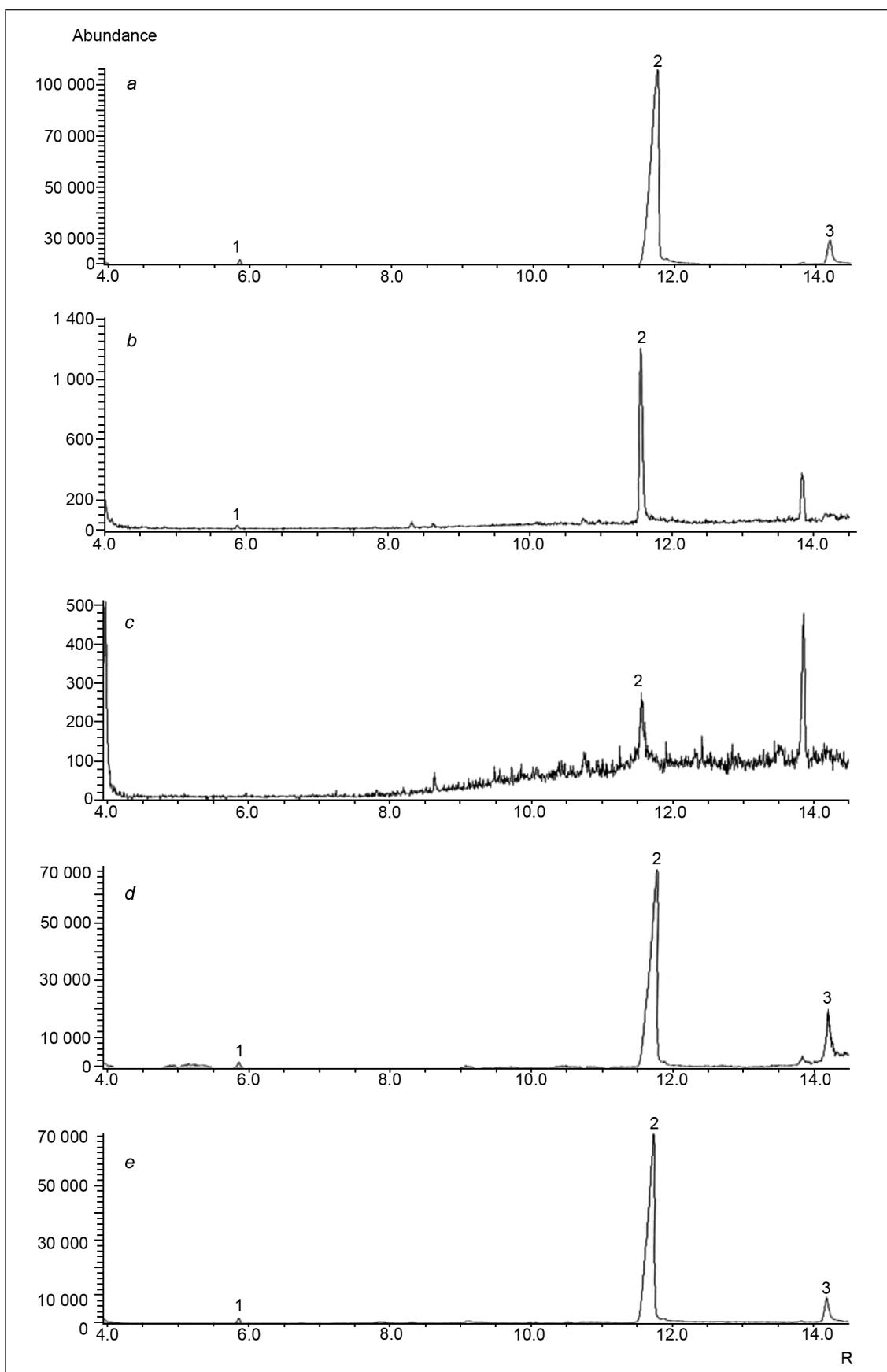
Fig. 6. GC/MS chromatogram of etheral extracts of 0.1 M NaOH + 5 mmol/l PMP solution (*a*), and the same solution after passing electric charge (Ah/l): 4.8 (*b*), 7.4 (*c*) using BDD anode, 4.8 (*d*), 7.4 (*e*) using Pt anode

of electrolyte decomposition results in the oxidation of about 94% of PMP on the BDD anode, presumably via electrogenerated hydroxyl radicals, and only of ~33% on the Pt anode. On the grounds of polarization and COD measurement data, a complete deactivation of the Pt electrode in the course of electrolysis was established.

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ELEKTROCHEMINĖ 1-FENIL-4-METIL-PIRAZOLIDONO OKSIDACIJA ANT BORU LEGIRUOTO DEIMANTO IR PLATINOS ELEKTRODŲ

S a n t r a u k a

Tirtos boru legiruoto deimanto (BLD) elektrodo galimybės elektrochemiškai oksiduoti 1-fenil-4-metil-pirazolidoną (FMP) vandeniniame tirpale, palyginti su tuo pačiu procesu, naudojant platinos elektrodą. Nustatyta, kad FMP šarminiame tirpale didina deguonies išsiskyrimo viršvoltažį ant BLD ir platinos elektrodų. Manoma, kad tai susiję su FMP arba jo skilimo produktų adsorbcija ant elektrodų. Elektrolizuojant šarminį FMP tirpalą elektrolito skilimo potencialų srityje, praleidus elektros kiekį, reikalingą esamam FMP kiekiui oksiduoti, ant BLD anodo suskaldoma apie 94 % FMP, matyt, dalyvaujant elektrogeneruotiems hidroksilo radikalams, ir tik apie 33 % FMP, naudojant platinos anodą. Tyrimų rezultatai leidžia daryti prielaidą, kad platinos elektrodą elektrolizės metu blokuoja FMP oksidacijos produktai.