ELECTROCHEMICAL OXIDATION OF LIMONENE

OXIDAÇÃO ELETROQUÍMICA DO LIMONENO

Alexandre D. Silva[1], Eliane D'Elia[1], Humberto R. Bizzo[1], Lúcio Cardozo-Filho[2] and O. A. C. Antunes[1*]

[1]Instituto de Química, Universidade Federal do Rio de Janeiro, CT Bloco A, Lab. 641, Rio de Janeiro, RJ 21945-970, Brasil
[2]Universidade Estadual de Maringá, Centro de Tecnologia, Departamento de Engenharia Química, Bloco D90, Av. Colombo 5790, Maringá, PR 87020-900, Brasil
[2]cardozo@deq.uem.br
*octavio@iq.ufrj.br

ABSTRACT

The electrooxidation of R(+)-limonene was carried out in acetic acid using p-Et$_4$NOTs as supporting electrolyte on platinum electrode at constant current (2.5, 5 and 10 mA) up to 2 F.mol^{-1} of charge. The influence of the additives LiCl and NaOAc was investigated. Depending on the reaction conditions, the following products were obtained: *cis*-carvyl acetate, *trans*-carvyl acetate, p-mentha-1,8-dien-3-ol acetate, perillyl acetate, p-menta-1,8-dien-2-ol acetate, α-terpinyl acetate, carvone, perilladehyde, *cis*-dihydrocarvone, *trans*-dihydrocarvone, *cis*-carveol, *trans*-carveol and p-cimenene. The products distribution changed in function of the current and additives. However, acetates were the predominant products. *trans*-Carvyl acetate is preferentially obtained in the presence of LiCl. The presence of NaOAc increased the overall faradaic yield. The solvation power of limonene by NaOAc could be responsible for this effect. However, in all the conditions investigated the overall faradaic yield was very low even in the NaOAc presence. This phenomenon can be related to the poor solubility of limonene in the reaction medium. The reaction products were identified based on their mass spectra and retention indexes.

Keywords: electrochemical oxidation, limonene, catalysis, retention index.

RESUMO

A eletrooxidação do limoneno foi efetuada em ácido acético, com o uso Et4NOTs como eletrólito de suporte, em um eletrodo de platina à corrente constante (2.5, 5 e 10 mA, até 2 F.mol-1). A influência de aditivos como LiCl e NaOAc foi investigada. Dependendo das condições usadas pode-se obter cis-acetato de carvila, trans- acetato de carvila, acetato de p-menta-1,8-dien-3-olila, acetato de perila, acetato de p-menta-1,8-dien-2-olila, acetato de α-terpinila, carvona, perilaldeído, cis-dihidrocarvona, trans-diidrocarvona, cis-carveol, trans-carveol e p-cimeneno. A distribuição dos produtos varia em função da corrente e dos aditivos, entretanto, os acetatos foram os principais produtos (artefatos). O trans-acetato de carvila foi preferencialmente obtido na presença de LiCl. O uso de NaOAc aumenta o rendimento faradaico que pode ser relacionado a solvatação do limoneno nestas condições. Entretanto, o rendimento faradaico foi baixo em todas as condições estudadas, mesmo na presença de NaOAc. Isto pode estar associado a uma baixa solubilidade do limoneno no meio reacional. Os produtos de reação foram identificados por seus espectros de massas e índices de retenção.

Palavras–chave: oxidação eletroquímica, limoneno, catálise, índices de retenção.

1 – INTRODUCTION

For the last years, our group has been successfully working on the catalytic oxidation of limonene and other monortepenes [1-6]. The choice of limonene as feedstock has been made due to the fact that this compound should provide an understanding of the regio- chemio- and stereoselectivity of the limonene oxidation reactions, associated to the fact that oxygenated derivatives of limonene are useful products for the perfumery, flavour and pharmaceutical industries. In this way significant efforts have been devoted to find synthetic methodologies to produce these compounds from these naturally abundant hydrocarbons in a cost-effective basis. *However, reasonable selectivities have been found very difficult to be achieved in the oxidation of limonene.* This fact prompted us to investigate the electrooxidation of limonene in order to have a full picture of the thermodynamical characteristics of the (catalytic) oxidation reaction besides an attempt to observe any possible selectivity. Anodic oxidation of limonene in aqueous solution has been described as not very promising because of the tendency of limonene to polimerize on the electrode surface [7]. As a consequence of this limitation, in some studies the oxidation of limonene have been carried out in non-aqueous media [8-12]. Methanol [8,9], tetrahydrofuran-water mixtures [10] and acetonitrile [11,12] have been used at constant potential, since it has been expected that the competition for electrode sites by organic solvent might reduce the tendency to polymerization of this compound.

Therefore, since the electrochemical oxidation of

Alexandre D. Silva, Eliane D'Elia , Humberto R. Bizzo, Lúcio Cardozo-Filho and O. A. C. Antunes

limonene must proceed analogously with general catalytic procedures when oxidation is carried out on organic media, the electrochemical reaction can be considered a good model to understand the outcome of the general catalytic oxidation reactions, that is, whether there was any thermodynamic difference in the electron transfer step which could drive the reaction selectively to a given product or the overall control of these reactions would be kinetic.

2 – EXPERIMENTAL

2.1 Materials

Carvone, perillaldeyde, *cis-* and *trans-*carveol,α-terpineol and the mixture *cis-* and *trans-*carveol were purchased from Aldrich. The mixture *cis-* and *trans-*carvyl acetate, perillyl acetate and α-terpinyl acetate were produced by acetylation (acetic anhydride, pyridine) respectively from the mixture *cis-* and *trans-*carveol, perillyl alcohol and α-terpineol.

*R-(+)-*Limonene (ALDRICH), tetraethylammonium *p*-toluenesulfonate (SIGMA-ALDRICH), glacial acetic acid (VETEC), anhydrous Na_2SO_4 (VETEC), ethyl acetate (VETEC) and dichloromethane (VETEC), acetic anhydride (VETEC) were used as received. Pyridine (Reagen) was distilled from CaH_2 prior to use.

High resolution gas chromatographic (HRGC) analyses were performed on a HP5890 gas chromatograph, with a 25 m capillary column (0.2 mm ID) coated with SE-54 (0.33 μm), and H_2 (1.0 mL/min, 333 K, 70 kPa) as carrier gas. The injector temperature was 493 K and detector temperature was 533 K. The oven temperature was increased from 333 K to 513 K at 5 K/min. The sample (1 μL) was injected in split mode (1:100 split ratio).

High resolution gas chromatographic-mass spectrometric (HRGC-MS) analyses were performed under the same chromatographic conditions using a HP5972 gas chromatograph-mass spectrometer, under electron impact (EI/70eV) or chemical ionization (CI/CH_4) modes. The ion source temperature was maintained at 503 K and the transfer line at 553 K.

2.2 Electrochemical measurements

The electrochemical oxidations were performed using potenciostat/galvanostat voltalab model 30 Radiometer. Electrolysis were carried out in a three-electrode electrochemical cell. The stationary platinum disk (1 cm^2) was used as working electrode. The saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrodes, respectively.

All the electrochemical measurements were performed at room temperature in a undivided glass cell filled with 9 mmol of tetraethylammonium *p*-toluenesulfonate (*p*-Et$_4$NOTs) used as a supporting electrolyte and 10 mmol of R(+)-limonene in 30 cm^3 solution of acetic acid.

2.3 Analytical Data

The products were identified by comparison of HRGC retention index and mass spectra fragmentation patterns with authentic synthetic standards. For spectral confirmations, commercial and synthetic compounds were co-injected on the GC column. However, whenever standard compounds were not available the identification was carried out by comparison with fragmentation database (NBS-Wiley) of the mass spectrometer. Other compounds have their structures proposed based on their mass spectra fragmentation patterns and those reported in the literature [4,12-15].

Quantitative analysis for the products was carried out by HRGC, with bromobenzene (PhBr) as internal standards.

2.4 Preparation of the mixture cis- and trans-carvyl acetate

The mixture *cis-* and *trans* carvyl acetate was prepared according to Reitsema [16] by treatment of the mixture *cis-* and *trans-*carveol (10 mmol), by acetic anhydride (53 mmol, 5 cm^3) in 1 cm^3 of pyridine for 2h15 min, under reflux and magnetic stirring at room temperature. At the end of the reaction, ethyl acetate was added, and this mixture was washed with aqueous HCl solution (1%). The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed leading to the mixture of *cis-* and *trans-*carvyl acetates. The same procedure has been followed to prepared perillyl acetate and α-terpinyl acetate. These compounds were synthesized for determination of their retention indices and mass spectra used in the identification and quantification analysis of the reactions products

2.5 General procedure for the preparation standard solutions

Solutions containing 10 mg of the standard substance and a known weight of PhBr used as internal standard were made up to 10 cm^3, with ethyl acetate. The resulting solution was used to quantify reaction products by HRCG.

2.6 General procedure for the electrochemical oxidation

A solution containing 10 mmol of the limonene and 9 mmol of *p*-Et$_4$NOTs in 30 cm^3 of acetic acid was added into a cell, equipped with a reflux condenser, and three electrodes. The electrolysis was carried out under a constant current (2.5 or 5 or 10 mA) and magnetic stirring at room temperature (25 ^{0}C). After 2 F.mol^{-1} of electricity was passed the solvent was removed under reduced pressure, the residue was added into a $NaHCO_3$ solution (5% in water), extracted with CH_2Cl_2 (3 x 20 cm^3), the organic phase was washed with water, dried over anhydrous Na_2SO_4 and finally filtered. The solvent was removed from the extract under reduced pressure. The residue was made up to 10 cm^3, with ethyl acetate. 100 μL of this solution was made up to 1 cm^3 with a known weight

of PhBr used as an internal standard. The resulting solution was analyzed by HRCG and HRCG-MS.

cis-Carvyl acetate **2**: MS m/z (relative intensity): 84(100%), 119(87), 109(77), 43(74), 152(59), 134(50), 93(29), 194(M$^+$); MS/CI(CH$_4$): 41(100%), 135 (84), 93(52), 107(44), 151(5), 79(1), 193(M$^+$+1), 194(M$^+$), 195(M$^+$+1); t$_R$=14,396 min; RI=1363.

trans-Carvyl acetate **3**: MS m/z (relative intensity): 109(100%), 119(98), 84(93), 43(92), 152(84), 91(63), 134(33), 194 (M$^+$); MS/CI(CH$_4$): 135(100%), 93(34), 107(32), 41(26), 151(3), 79(1), 193(M$^+$+1), 194(M$^+$), 195(M$^+$+1); t$_R$=13,718 min; RI=1338.

cis/trans- p-Mentha-1,8-dien-3-ol acetate **4** :

4a: MS m/z (relative intensity): 84(100%), 152(28), 43(24), 119(18), 91(13), 194 (1, M$^+$); MS/CI(CH$_4$): 135(100%), 41(27), 107(26), 93(20), 151(2), 43(1), 193(M$^+$+1), 194(M$^+$), 195(M$^+$+1);t$_R$=13,542 min; RI=1332.

4b: MS m/z (relative intensity): 84(100%), 134(54), 43(32), 119(28), 91(20), 152 (19), 194 (0.1, M$^+$); MS/CI(CH$_4$): 135(100%), 41(26), 107(23), 93(15), 43(4), 151(2), 193(M$^+$+1), 194(M$^+$), 195(M$^+$+1); t$_R$=13,771min; RI=1340.

Perillyl acetate **5**: MS m/z (relative intensity): 43(100), 91(75), 68(50), 119 (49), 79(37), 134(31), 152(22), 194(M$^+$); t$_R$=13,326 min; RI=1436.

p-Menta-1,8-dien-2-ol acetate **6**: MS m/z (relative intensity): 109(100), 43(97), 152(27), 93(25), 71(24), 67(23), 41(17), 194(M$^+$); 153(100%), 135(51), 195(17,M$^+$+1), 107(12), 154(10), 93(10), 109(8), 43(7); t$_R$=17,260 min; RI=1473.

α-Terpinyl acetate **7**: MS m/z (relative intensity): 121(100), 43(76), 93(73), 136 (56), 59(17), 79(18), 107(13); MS/CI(CH$_4$): 137(100%), 81 (34), 41(32), 61(6), 121(3), 43(3), 195(M$^+$-1); t$_R$=14,039 min; RI=1352.

Carvone **8**: MS m/z (relative intensity): 82(100%), 54(43), 93(33), 108(32), 150(7, M$^+$), 135(4); t$_R$=11,166 min; RI=1245.

Perilladehyde **9**: MS m/z (relative intensity): 68(100%), 79(82), 107(53), 53(45), 122(34), 135 (38), 150 (20, M$^+$); t$_R$=12,008 min; RI=1275.

cis-Dihydrocarvone **10**: MS m/z (relative intensity): 67(100%), 95(70), 82(47), 109(35), 108(22), 152(18, M$^+$), 150 (20, M$^+$); t$_R$=9,895 min; RI=1195.

trans-Dihydrocarvone **11**: MS m/z (relative intensity): 67(100%), 95(80), 82(43), 152(29, M$^+$), 53(22), 109 (21), 137(13) ; t$_R$=10,099 min; RI=1203.

trans-Carveol **12**: MS m/z (relative intensity): 109(100%), 84(60), 55(33), 91(25), 67(20), 119(15), 134(3), 152(1, M$^+$); t$_R$=10,496 min; RI=1219.

p-cimeneno **13**: MS m/z (relative intensity): 132(100%, M$^+$), 117(98), 115(55), 91(45), 92(20), 65(15), 118(9), 101(4); t$_R$=7,065 min; RI=1090.

Unknown compound **14**: MS m/z (relative intensity): 43(100%), 82(50), 71(46), 67(46), 109(35), 137(28), 152(26); t$_R$=16,503 min; RI=1444.

Unknown compound **15**: MS m/z (relative intensity): 43(100%), 82(64), 71(42), 67(42), 109(26), 137(13), 152 (10), 194(2); t$_R$=16,445 min; RI=1442.

Unknown compound **16**: MS m/z (relative intensity): 43(100%), 91(60), 109(59), 119(44), 134(31), 152(30), 79 (28), 84(14); t$_R$=14,208 min; RI=1357.

Unknown compound **17**: MS m/z (relative intensity): 43(100%), 91(98), 119(94), 134(75), 93(59), 109(57), 152 (35), 194(0.3); t$_R$=13,014 min; RI=1311.

Unknown compound **18**: MS m/z (relative intensity): 43(100%), 67(48), 82(47), 93(38), 109(29), 134(24), 152(14), 194(2); t$_R$=16,302 min; RI=1436.

Unknown compound **19**: MS m/z (relative intensity): 43(100%), 135(65), 93(60), 127(56), 107(27), 68(25), 170 (21, M$^+$), 172(7, M$^+$); MS/CI(CH$_4$): 135(100%), 41(24), 93(22), 107(17), 171(8,M$^+$+1), 169(1,M$^+$-1), 170(1,M$^+$); t$_R$=16,213 min; RI=1433.

Unknown compound **20**: MS m/z (relative intensity): 71(100%), 43(55), 108(42), 93(33), 135(27), 170(9), 152(3), 172 (3), 188(3), 190 (1); t$_R$=13,489 min; RI=1330.

Unknown compound **21**: MS m/z (relative intensity): 93(100%), 135(97), 91(38), 67(35), 171(12), 173 (4), 207(2, M$^+$), 210(2, M$^+$); t$_R$=11,946 min; RI=1304.

3 – RESULTS AND DISCUSSION

The limonene electrochemical oxidation was carried out using the galvanostatic mode, i.e., at fixed current value, where three current values (2.5, 5 and 10 mA) were applied. It was investigated the influence of lithium chloride (LiCl) and sodium acetate (NaOAc) only for 10 mA. Depending on the reaction conditions the following products were obtained: *cis*-carvyl acetate **2**, *trans*-carvyl acetate **3**, mixture *cis*- and *trans* p-mentha-1,8-dien-3-ol acetate **4**, perillyl acetate **5**, *p*-menta-1,8-dien-2-ol acetate **6**, α-terpinyl acetate **7**, carvone **8**, perilladehyde **9**, *cis*-dihydrocarvone **10**, *trans*-dihydrocarvone **11**, *trans*-carveol **12** and *p*-cimenene **13**. The table 1 shows the distribution of reaction products. The distribution of the allylic compounds in function of current changed only at 2,5 mA.

Isomerization of limomene was observed in medium acid, this process occurs through the formation of a carbenium ion [17] that lead to formation of α-terpinyl acetate by nucleophilic attack of acetic acid.

The isomerization of limonene was observed in all galvanostatic oxidation reactions, since α-terpinyl acetate was obtained in the five studied reactions. In the mixture *cis*- and *trans*-carvyl acetate the isomer *trans* is preferably obtained in all reactions conditions. These results showed a stereoselectivity in the nucleophilic addition to the limonene. We can explain this behavior by the adsorption through in one of the sides of the double bond. The distribution of allylic acetate changed in the presence of LiCl. The mixture *cis*- and *trans*-carvyl acetate was obtained selectively, showing 41 % of *trans*-carvyl acetate. The concentration of carvone was decreased in the presence of NaOAc, being this compound not observed in the presence of LiCl.

Alexandre D. Silva, Eliane D'Elia , Humberto R. Bizzo, Lúcio Cardozo-Filho and O. A. C. Antunes

Table 1. Distribution of Products (%)[a] in Electrooxidation of Limonene[a]

I/mA	2	3	4a	4b	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
2.5	8	30	3	-	8	8	20	10	-	8	-	-	-	8	-	-	-	-	-	-	-
5	5	20	18	6	6	6	15	7	6	6	-	-	5	6	-	-	-	-	-	-	-
10	6	20	24	8	7	6	5	11	-	-	5	5	-	8	-	-	-	-	-	-	-
10[c]	6	21	23	11	8	9	1	2	-	3	-	-	-	6	1	2	5	-	-	-	-
10[d]	10	41	-	-	-	2	7	-	4	-	-	-	8	-	-	-	-	3	9	6	4

[a]Determined by HRGC relative areas.[b]Conditions: 10mmol limonene, [c]10mmol NaOAc. [d]10mmol LiCl, 2F.mol^{-1}, 295K, 9mmol *p*-Et$_4$NOTs in 30cm^3 of acetic acid, under magnetic stirring.
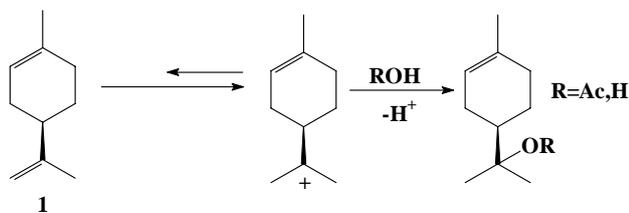
Scheme 1.

The overall faradaic yield is 3% in presence of NaOAc and 1% in other conditions, so it can be related to the poor solubility of limonene in the reaction medium. However, the faradaic yield is higher in the presence of NaOAc, presumably due to its interaction with limonene.

From the studies of cycloalkene oxidation lead by Shono and Ikeda [18], we propose that the limonene oxidation occurs according to the scheme 2. The formation of *cis*- and *trans*- carvyl acetate could occur through the radical species generated by anodic oxidation of the acetic acid (I), that starts the reaction by the abstraction of the allylic hydrogen from limonene (II). Then, the radical suffers an anodic one-electron oxidation (III), to the cation which, *in situ*, suffers the nucleophilic attack of the solvent (IV). This process takes place on the electrode surface, after the adsorption of those species. This same scheme can be applied to the other allylic acetates.
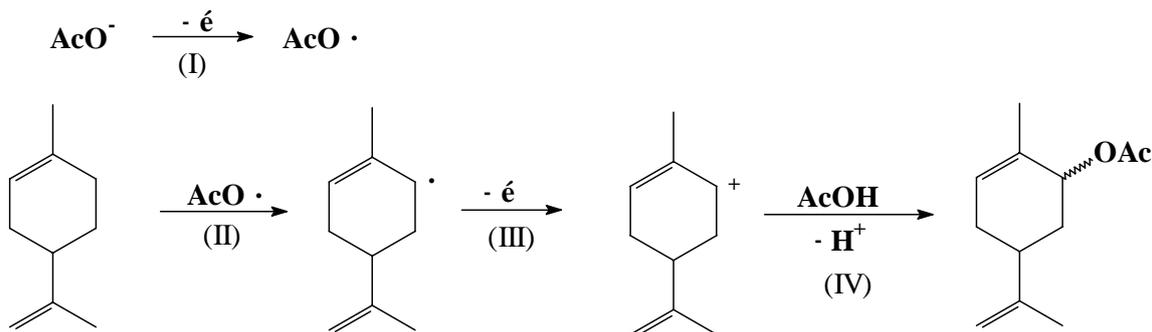
Scheme 2.
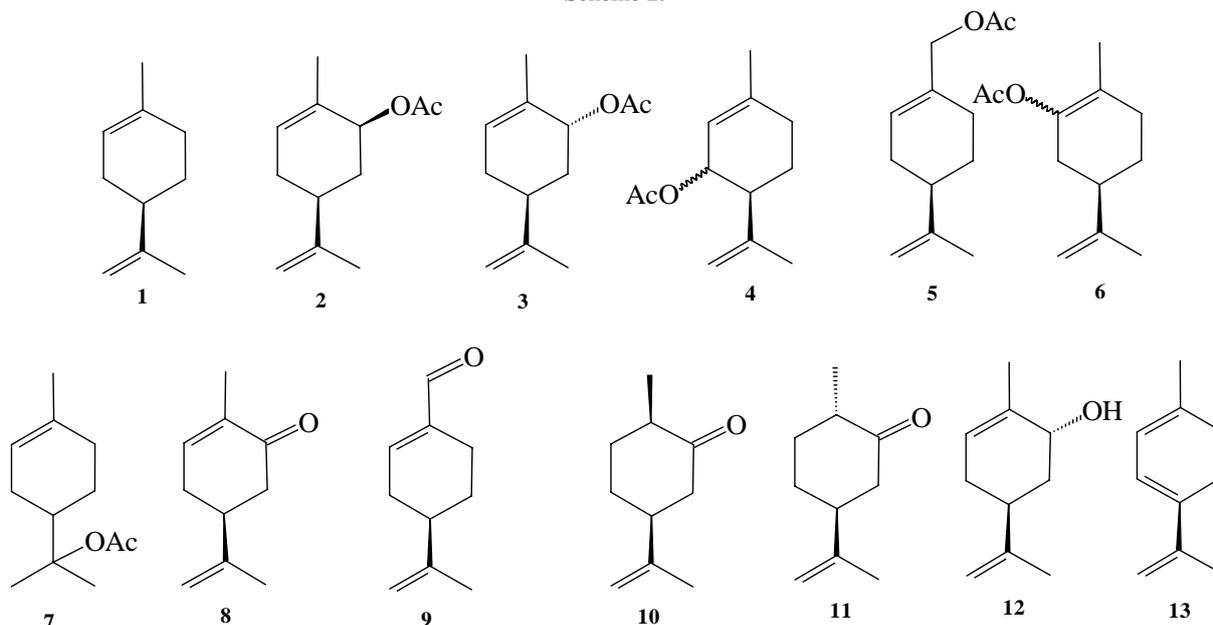
Figure 1

As can be seen in figure 1 the predominant reaction products arose from allylic oxidation, including the *cis*- and *trans* mixture of acetate **4**.

The structures of these compounds were based on mass spectral data. The EI mass spectrum of the acetate showed the molecular ion m/e 194 ($C_{12}H_{18}O_2$) and the base peak m/e 84. This signal is the base peak of *cis*-carvyl acetate **2**, an isomer of the proposed structure. It's possible that the production of the most abundant ion (m/e 84) arise from the elimination of one neutral molecule of ketene ($CH_2=C=O$) from molecular ion. In this process the radical cation carveol (m/e 152) was formed, followed by the rupture of the link which is alpha to the carbonyl group and fission of the doubly allylic carbon-carbon bonds of radical cation carveol. In the CI system the GC carrier gas also serve as the CI reagent gas. The CI mass spectrum of acetate shows the signals m/e 194 (M^+), m/e 195 (M^++H) and m/e 195 (M^+-H) attributed to chemical ionization using methane as carrier gas. The last fragment is due to the loss of molecule water from the protonated radical cation carveol. Such data led us to propose above structure.

4 – CONCLUSIONS

The galvanostatic oxidation favored products from allylic oxidation of endocyclic double bond and showed stereoselectivity *trans*. In the mixture *cis*- and *trans*-carvyl acetate the isomer *trans* is preferably obtained in all the reactions conditions. The distribution of allylic acetate changed in the presence of LiCl. The mixture *cis*- and *trans*-carvyl acetate was obtained selectively, showing 41 % of *trans*-carvyl acetate. The overall faradaic yield is low in all studied reactions probably due to the poor solubility of limonene in the reaction medium. In the presence NaOAc it was observed the best faradaic yield value (3%). This result was related to the solvation power of limonene by NaOAc.

ACKNOWLEDGMENTS

REFERENCES

[1] C.M. Rezende, D. Sc. thesis, NPPN-UFRJ, Rio de Janeiro, RJ, Brazil, 1992.
[2] M. F. T. Gomes, O. A. C. Antunes: Cat. Lett. **38**, 133 (1996).
[3] M. F. T. Gomes, O. A. C. Antunes: Cat. Lett. **42**, 213 (1996).
[4] M. F. T. Gomes, O. A. C. Antunes: J. Mol. Catal. A: Chem. **121**, 145 (1997).
[5] M. Gomes Jr., O. A. C. Antunes: Catal. Commun. **2**, 225 (2001).
[6] A. D. Silva, M. L. Patitucci, H. R. Bizzo, E. D'Elia, O. A. C. Antunes: Catal. Commun. **3**, 435 (2002).
[7] J. B. Reed, J.E. Hawkins: J. Electrochem. Soc. **99**, 178 (1950).
[8] T. Shono, A.Ikeda, J. Hayashi, S. Hakozaki: J. Am. Chem. Soc. **97**, 4201 (1975).
[9] J.A. Caram, M.E. Martins, E.G. Gros, C.M. Marschoff: Electrochim. Acta **35**, 1163 (1990).
[10] V. Montiel, M. López-Segura, A. Aldaz, M. Grande, F. Barba: Electrochim. Acta **29**, 1123 (1984).
[11] J.A. Caram, M.E. Martins, E.G. Gros, C.M. Marschoff: Electrochim. Acta **35**, 497 (1990).
[12] J.A. Caram, M.E. Martins, E.G. Gros, C.M. Marschoff: Electrochim. Acta **66**, 1757 (1988).
[13] R.P. Adams: *Identification of Essencial Oil Components by Gas Chromatography/Mass Spectroscopy*. Allured Publishing Corporation .1995.
[14] R.M. Silverstein, A.A. Swingar: *Monoterpenos - Infrared, Mass, ^1H NMR, and ^{13}C NMR Spectra, and Kováts Indices*. Aldrich Chemical Company, INC. 1981.
[15] E. V. Shydow: Acta Chem. Scand. **19**, 2083 (1964).
[16] R.H. Reitsema: J. Am. Chem. Soc. **75**, 196 (1953).
A.F. Thomas, Y. Bessière: Nat. Prod. Rep. **6**, 291 (1989).
18. T. Shono, A. Ikeda, J. Hayashi: J. Am. Chem. Soc. **94**, 7892 (1972).