



Electrochemical selective oxidation of aromatic alcohols with sodium nitrate mediator in biphasic medium at ambient temperature

C. Christopher^a, S. Lawrence^b, M. Anbu Kulandainathan^c, K. Kulangiappar^c, M. Easu Raja^d, N. Xavier^d, S. Raja^{d,*}

^a Department of Chemistry, Thanthai Hans Roever College, Perambalur 621 212, India

^b Department of Chemistry, Sacred Heart College, Tirupattur 635 601, India

^c Electroorganic Division, Central Electrochemical Research Institute, Karaikudi 630 006, India

^d Department of Chemistry, St. Joseph's College, Tiruchirappalli 620 002, India

ARTICLE INFO

Article history:

Received 13 January 2012

Revised 23 March 2012

Accepted 25 March 2012

Available online 4 April 2012

Keywords:

Electrochemical selective oxidation

Aromatic alcohols

Biphasic electrolysis

Sodium nitrate mediator

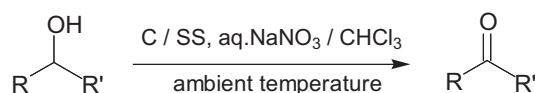
ABSTRACT

Sodium nitrate was used as an effective redox mediator in the electrochemical oxidation of primary and secondary aromatic alcohols in biphasic electrolysis at ambient temperature. The oxidation reactions were carried out in an undivided cell equipped with carbon anode and stainless steel cathode in which upper aqueous phase contained 0.83% sodium nitrate with minimum amount of HCl whereas, the lower organic phase consisted of aromatic alcohols in chloroform. A variety of aromatic alcohols were efficiently oxidized to aldehydes and ketones in good yields with maximum selectivity (>99%).

© 2012 Elsevier Ltd. All rights reserved.

The transformation of alcohols into corresponding carbonyl compounds is one of the simplest and fundamental reactions in organic synthesis.¹ In particular, aldehydes represent an important class of products and versatile intermediates in the field of fine chemicals such as fragrances or food additives.² Generally, alcohol oxidation requires stoichiometric amounts of toxic heavy metal salts³ or expensive catalysts containing transition metals.^{4–10} Most of these inorganic oxidants create an environmental problem by producing large amount of 'spent reagent' and hence the process is not eco-friendly. The catalytic oxidation of alcohols with molecular oxygen using transition metal salts^{11–18} and polyoxometalates^{19,20} is also reported in the literature. At present, only a few reports are available related to environmentally benign reagents such as silica-supported reagents²¹ and carbon-supported platinum catalysts²² for the synthesis of aldehydes.

In recent years, electro organic synthesis has also paved a new way to green chemical processes by introducing environmentally benign reagents compared to conventional redox reactions. However, the reactions involving nitroxyl radical compound-mediated processes used costly catalyst along with mediators in the electrochemical oxidation of alcohols.^{23–25} Moreover, in homogeneous electrolysis system, mixture of products is obtained due to over



R = Phenyl, Substituted phenyl, benzyl, Ph-CH=CH-

R' = H, alkyl Carbon anode(C) / (SS) Stainless Steel cathode

Scheme 1. Selective oxidation of aromatic alcohols in biphasic electrolysis.

oxidation of reactant on electrode surface which leads to lower selectivity. In the case of emulsion electrolysis, electrode passivation leads to higher current density and consumes more electrical energy. The above said two systems may pose problem in the separation of spent mediator at the end of the reaction but biphasic electrolysis offers obvious advantages over homogeneous electrolysis with respect to easy handling and mediator recycling.²⁶

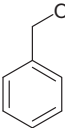
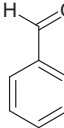
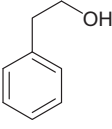
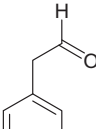
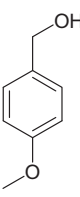
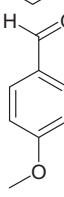
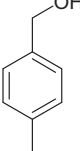
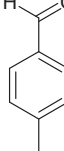
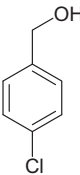
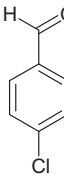
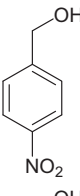
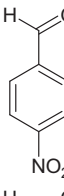
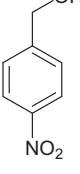
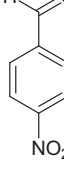
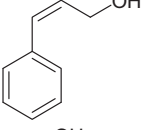
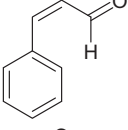
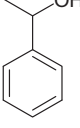
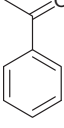
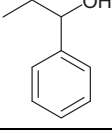
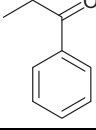
Presently, only a few reports are available on the syntheses of fine chemicals by biphasic electrolysis method.^{27,28} Recently, we developed a biphasic electrolysis system involving electrochemical oxidation of benzyl alcohol to benzaldehyde mediated by sodium nitrate at ambient temperature.²⁹ The current work focuses on the selective oxidation of aromatic alcohols using the optimized reaction conditions (Scheme 1).³⁰

The primary and secondary alcohols were oxidized to corresponding aldehydes and ketones, respectively. Interestingly,

* Corresponding author. Tel.: +91 9443141407; fax: +91 0431 2701501.

E-mail address: chrishemo@gmail.com (S. Raja).

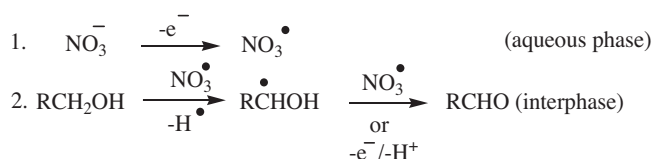
Table 1
Electrochemical selective oxidation of aromatic alcohols in biphasic medium

Entry	Alcohols	Product	Yield ^a (%)	Faraday	Current efficiency (%)
1			95	2	95.0
2			63	4	31.5
3			72	2	72.0
4			85	2	85.0
5			81	4	40.5
6			10	4	05.0
7 ^b			44	4	22.0
8			71	4	37.0
9			75	2	75.0
10			32	4	16.0

Biphasic electrolysis conditions: current density = 50 mA/cm²; electrodes = carbon/stainless steel; temperature = ambient temperature (30–34 °C); stirring rate = 50 rpm; aqueous layer = 0.83% NaNO₃ + 0.37 M HCl (60 ml); organic layer = alcohols (10 mmol) dissolved in chloroform (20 ml).

^a Selectivity >99% in each entry.

^b Reaction (entry 7) was carried out in acetonitrile solvent (homogeneous electrolysis) as the alcohol has low solubility in chloroform.



Scheme 2. Carbon-centered radical mechanism.

further oxidation to acid was minimized in this biphasic electrolysis system. The results are summarized in Table 1. The product aldehydes or ketones were determined by HPLC. Authentic samples were used to calculate the peak area of the corresponding experimental products for yield calculation. The alcohols and other reagents were purchased from Sigma–Aldrich, Alfa-Aesar, & Merck. They were used without further purification.

Sodium nitrate was chosen as a cheaper redox mediator to carry out the selective oxidation of aromatic alcohols effectively in biphasic electrolysis. In the aqueous phase one electron oxidation³¹ of nitrate ion allows in situ generation of nitrate radical which is known to be an efficient hydrogen abstractor.³² Electrochemically generated nitrate free radical reacts with aromatic alcohol at the interphase region of the organic and aqueous phases selectively to offer aldehyde or ketone. Finally, the nitrate radical can be effectively regenerated at carbon anode after reaction with alcohol. After completion of the electrolysis, separation of organic phase and evaporation of the organic solvent afford the product.

Electrochemical selective oxidation of benzyl alcohol was effectively carried out in biphasic system with 2 F/mol of charge which resulted in excellent yield (95%). Using this biphasic system aromatic alcohol and substituted aromatic alcohols were oxidized to the corresponding carbonyl compounds at room temperature in a single compartment cell in high yields (Scheme 1).³⁰ The yields of the products are listed in Table 1. We observed a smooth oxidation of aromatic alcohols substituted with electron-donating groups such as -methoxy, -methyl groups (entries 3 and 4) yielding 72% and 85%, respectively with 2 F/mol current, while alcohols substituted with electron-withdrawing group such as -chloro (entry 5) required 4 F/mol of electricity with a maximum yield of 81%. The strong electron-withdrawing group such as -nitro, substituted aromatic alcohol (entry 6) gave only 10% aldehyde due to its poor solubility in chloroform solvent. When the same oxidation was conducted in homogeneous condition (CH₃CN as solvent) 44% yield of 4-nitrobenzaldehyde was obtained (entry 7). Among the secondary alcohols (entries 9 and 10) 1-phenyl ethanol gave higher yield (75% yield with 2 F/mol current) than the 1-phenyl propanol (32% yield with 4 F/mol current). Probably the presence of additional methyl group may have hindered the bulky nitrate radical to come closer to the benzylic hydrogen—hence the yield was poor. In all the above entries 1–10 the selectivity was observed >99%.

A possible mechanism for the electrochemical selective oxidation of aromatic alcohols in biphasic medium is proposed in Scheme 2 as cited in literature.³³

In conclusion, sodium nitrate mediator, carbon, and stainless steel electrodes are cheaper reagents that were employed in the selective oxidation of aromatic alcohols in biphasic electrolysis at ambient temperature. This method brings more advantages than homogeneous systems with respect to easy handling, atom utility, and reuse of spent mediator. The selectivity was observed greater than 99% in all oxidation reactions. The biphasic electrolysis set up is so simple that the reactions can be carried out at room temperature compared with the conventional oxidation reactions. On the whole, the proposed electrochemical process and reaction set up are simple and contribute to an extent as a greener synthesis.

Acknowledgments

We are thankful to Dr. T.K. Krishnamoorthy, Former Principal, A.V.V.M. Sri Pushpam College, Thanjavur 613503, India, for his valuable guidance. Our special thanks to Mr. J. Sebastian Raja, Institute of Physical Chemistry ‘Rocasolano’, Department of Biophysical Chemistry, Madrid 28006, Spain, for his generous support and encouragement to carry out this work.

References and notes

- Sheldon, A.; Kochi, J. K. *Metal Catalysed Oxidations of Organic Compounds*; Academic Press: London, 1981.
- Musawir, M.; Davey, P. N.; Kelly, G.; Kozhevnikov, I. V. *Chem. Commun.* **2003**, 1414–1415.
- Trahanovsky, W. S. In *Oxidation in Organic Chemistry*; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1978.
- Zhan, B.-Z.; White, M. A.; Sham, T.-K.; Pincock, J. A.; Doucet, R. J.; Ramana Rao, K. V.; Robertson, K. N.; Stanley Cameron, T. J. *Am. Chem. Soc.* **2003**, 125, 2195.
- Ji, H.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2002**, 43, 7179.
- Gamez, P.; Aubel, P. G.; Driessen, W. L.; Reedijk, J. *Chem. Soc. Rev.* **2001**, 30, 376.
- Skibida, I. P.; Sakharov, A. M. *Catal. Today* **1996**, 27, 187.
- Wolfson, A.; Wuyts, S.; De Vos, D. E.; Vankelecom, I. F. J.; Jacobs, P. A. *Tetrahedron Lett.* **2002**, 43, 8107.
- Li, J. W.; Sun, W.; Xu, L. W.; Xia, C. G.; Wang, H. W. *Chinese Chem. Lett.* **2004**, 15, 1437.
- Chhikara, B. S.; Tehlan, S.; Kumar, A. *Synlett* **2005**, 63.
- Reddy, S. R.; Das, S.; Punniyamurthy, T. *Tetrahedron Lett.* **2004**, 45, 3561.
- Iwahama, T.; Yoshino, Y.; Keitoku, T.; Sakaguchi, S.; Ishii, Y. J. *Org. Chem.* **2000**, 65, 6502.
- Marko, I. E.; Guaiter, A.; Dumeunier, R.; Doda, K.; Philippart, F.; Brown, S. M.; Ureh, J. *Angew. Chem., Int. Ed.* **2004**, 43, 1588.
- Velusamy, S.; Ahmed, M.; Punniyamurthy, T. *Org. Lett.* **2004**, 6, 4821.
- Egami, H.; Onitsuka, S.; Katsuki, T. *Tetrahedron Lett.* **2005**, 46, 6049.
- Martin, J.; Martin, C.; Faraj, M.; Bregeault, M. *Nouv. J. Chim.* **1984**, 8, 141.
- Schultz, M. J.; Hamilton, S. S.; Jensen, D. R.; Sigman, M. S. *J. Org. Chem.* **2005**, 70, 3343.
- Yoshida, Akihiro; Takahashi, Youichi; Ikeda, Tsuyoshi; Azemoto, Kazuki; Naito, Shuichi *Catal. Today* **2011**, 164, 332.
- Biradar, Ankush V.; Dongare, Mohan K.; Umbarkar, Shubhangi B. *Tetrahedron Lett.* **2009**, 50, 2885.
- Bordoloi, Ankur; Sahoo, Suman; Lefebvre, F.; Halligudi, S. B. *J. Catal.* **2008**, 259, 232.
- Wiles, Charlotte; Watts, Paul; Haswell, Stephen J. *Tetrahedron Lett.* **2006**, 47, 5261.
- Korovchenko, Pavel; Donze, Cécile; Gallezot, Pierre; Besson, Michele *Catal. Today* **2007**, 121, 13.
- Liaigre, D.; Breton, T.; Mustapha Belgsir, E. I. *Electrochem. Commun.* **2005**, 7, 312.
- Yusuke, J.; Koichi, M. S.; Tanaka, H. *Tetrahedron Lett.* **2005**, 46, 8975.
- Tanaka, H.; Kawakami, V.; Goto, K.; Kuroboshi, M. *Tetrahedron Lett.* **2001**, 42, 445.
- Forsyth, S. R.; Pletcher, D. *Extended Abstracts of the 1st International Symposium on Electroorganic Synthesis*, Kurashiki, 1986, p 35.
- Sripriya, R.; Chandrasekaran, M.; Noel, M. J. *Appl. Electrochem.* **2008**, 38, 597.
- Raynal, F.; Barhdadi, R.; Périchon, J.; Savall, A.; Troupel, M. *Adv. Synth. Catal.* **2002**, 344, 45.
- Christopher, C.; Lawrence, S.; John Bosco, A.; Xavier, N.; Raja, S. *Catal. Sci. Technol.* **2012**, 2, 824.
- Representative procedure for the electrochemical selective oxidation of benzyl alcohol*: A solution of benzyl alcohol (Table 1, entry 1) {1.08 g 10 mmol} in 20 ml chloroform was taken in a beaker type undivided cell. To the above solution a 0.83% sodium nitrate solution containing 2 ml of HCl (36.5% solution) was added. The carbon anode (15 cm²) and stainless steel cathode (15 cm²) were placed in the upper aqueous phase. The organic phase alone was stirred with a magnetic stirrer at a rate of 50 rpm in such a way that the organic phase does not touch the electrodes. The electrolysis was conducted galvanostatically at a current density of 50 mA/cm² until the quantity of charge indicated in Table 1 was passed. The electrolysis was monitored by HPLC (Shimadzu) using a shimpack ODS-18 column (250 mm × 4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (80:20) at a flow rate of 1 ml/min. Samples including authentic samples were analyzed using UV detector at a wavelength of 254 nm. After completion of electrolysis, the organic phase was separated, washed with water (2 × 25 ml), dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure to afford 1.13 g of crude benzaldehyde. The HPLC analysis of the residue showed 95% purity.
- Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, NY, 1970.
- Scholl, P. C.; Lentsch, S. E.; Van De Mark, M. R. *Tetrahedron* **1976**, 32, 303.
- Leonard, J. E.; Scholl, P. C.; Steckel, T. P. *Tetra Tetrahedron Lett.* **1980**, 21, 4695.