Anal. Bioanal. Electrochem., Vol. 15, No. 7, 2023, 587-602
https://www.doi.org/10.22034/abec.2023.706511

Analytical &
Bioanalytical
Electrochemistry

2023 by CEE
www.abechem.com

Full Paper

The Highly Effective Electrochemical Oxidation of Substituted Benzyl Alcohols in A Biphasic Medium Is Mediated by Bromate on A Platinum Electrode

Susila G. Savari, and S. Joseph Selvaraj*

Department of Chemistry, St. Joseph's College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli-620 002, Tamilnadu, India

*Corresponding Author, Tel.: +91-7001941894
E-Mail: sjc_selvaraj@yahoo.com

Received: 12 April 2023 / Received in revised form: 4 July 2023 /
Accepted: 19 July 2023 / Published online: 31 July 2023

Abstract- This article describes how benzyl alcohol was electro-oxidatively converted to benzaldehyde at a platinum metal electrode in a biphasic media utilizing bromate as the mediator. Based on current density, electrode material, temperature, solvent, inorganic salt mediator, and reaction system pH, electrolysis conditions were tuned. By adjusting the electrolysis parameters coupled with a straightforward reaction setup, the current experiment was able to produce outstanding yields of benzaldehyde (97%) at the optimal reaction conditions. One mole of benzyl alcohol was converted to benzaldehyde using 5 F of electrical current. The yield (97%) and current efficiency (97%) of two-phase electrolysis are both quite high. Several substituted benzyl alcohols were subjected to the optimum conditions, and encouraging yields were achieved. The oxidation of benzyl alcohol has been theorized to be a feasible mechanism. To the best of our knowledge, our work is the first to describe how substituted benzyl alcohol derivatives are oxidized in a biphasic system. In the current study, a number of primary and secondary alcohols were converted to the matching aldehydes or ketones by using the mediator bromate.

Keywords- Electrooxidation; Sodium bromate; Substituted benzyl alcohols; Platinum electrode; Biphasic medium

---

1. INTRODUCTION

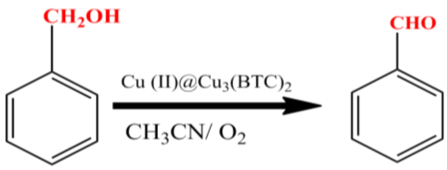
It is well known that one of the most significant issues in organic synthesis, as well as industrial and medicinal chemistry, is the production of carbonyl compounds from alcohol. A diverse range of natural products and bioactive chemicals are assembled using carbonyl compounds as important intermediates [1]. Nonetheless, one of the most fundamental and significant reactions in synthetic organic chemistry is the oxidation of alcohols to the corresponding carbonyl molecules. Since they are essential building blocks for pharmaceuticals, dyes, and fine compounds, this subject has received a lot of interest in chemical research during the past few decades [2,3]. Platinum anode and platinum pole have been used to study the two-phase electrolysis of benzyl alcohol and benzaldehyde.

It has been possible to produce benzaldehyde with a high yield (97%) and high current efficiency (97%) [4]. There have been reports of the employment of NO_3^-/NO as redox mediators for the conversion of various primary and secondary alcohols [5]. The electrochemical oxidation of alcohol to aldehydes or ketones is currently mediated by BrO_3^-/BrO_4^-. After electrolysis is finished, the organic layers are separated and evaporated to produce products. Pletcher et al. report on the advantages of double electrolysis as a feasible method for organic synthesis [6]. Many studies have employed potassium dichromate to oxidize various organic compounds under various aqueous acidic conditions [7], but several of these techniques have drawbacks such as high reaction temperatures, excessive primary alcohol oxidation to carboxylic acids, and protracted reaction times, low product yields and time-consuming processes sometimes.

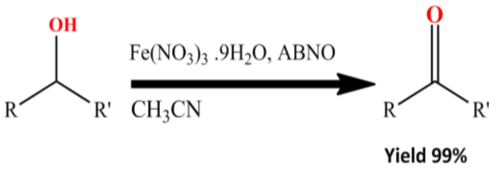
Recently achieved outstanding yields from the electrooxidation of alcohols utilizing gold complex as the electrocatalyst under clean circumstances [8]. The aforementioned techniques, however, are severely constrained by factors including difficult experimental circumstances, inexpensive goods, high temperatures, and a shortage of electricity [9-12]. To solve these issues, a green energy source is needed to better drive the electro-organic process. As a result, it is strongly recommended to use electric current in alcohol transformation reactions [12]. Direct electro-organic functionalization has gained popularity in recent years and is a crucial synthetic tool for organic oxidation and reduction reactions [12,13]. In comparison to traditional homogeneous procedures, electro-organic synthesis offers a greener alternative; in particular, it does so by avoiding the use of significant amounts of toxic or corrosive reagents [14]. Electro-organic synthesis showed superior benefits over the usual conventional approaches. Furthermore, using a biphasic medium has a number of benefits for practical organic synthesis [15-19]. The most notable aspect is the electron transfer mechanism, which is crucial in creating a radical intermediate in a substance that acts as a "mediator" between the working electrode and substrate [20]. The electron transfer mediators have established themselves as a crucial mechanism for preventing unfavorable side effects [21,22]. As a result, numerous appealing transformations have been widely used for this established methodology, including coupling reactions [23,24] and dehalogenation reactions. This practice has been more appealing in recent years because of the more affordable and environmentally friendly technology [25]. We recently created a straightforward electrochemical approach for producing radical species directly from straightforward benzyl alcohols, where the bromate radical intermediate was synthesized in situ and with great precision using electrochemistry [26]. Platinum is a noble metal that has a high degree of stability and corrosion resistance. Like Au, it is frequently used to produce jewelry due to its stability. It serves as an electrode to oxidize organic materials, produce hydrogen, or decrease oxygen.

Platinum is used in an electrochemical cell because it is resistant to oxidation. Platinum electrodes are considered inert because, in the systems where they are used, they do not participate in any chemical reactions at all. Platinum electrodes are used in laboratories for quantitative electrochemical analysis. The electrode materials are not used up or supplemented. The advantage of this work bromates radical intermediate produced good to exceptional yields when it oxidized the substrates. As a result, utilizing readily available, straightforward substrates, we offer here a novel method for coupling the derivatives of benzyl alcohol oxidations in biphasic electrolysis and related scaffolds.

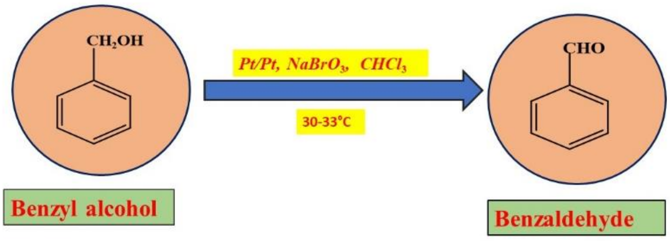
a) S. Zhang and Co-Workers



b) G. Wang and Co-workers



c) Present work



Scheme 1. Electrocatalytic oxidation of Benzyl alcohol

The surprising aspect of this technique is the ease with which a substrate that has been inhibited can also be changed by selective transformations. Moreover, it exhibits good current efficiency, utilizes all of the atoms, and prevents the production of side products. To the best of our knowledge, our work is the first to describe how substituted benzyl alcohol derivatives are oxidized in a biphasic system. In addition, a number of literature publications assert that transition metal catalysts such Co, Cu, Ir, Pd, Mo, and V have been extensively used for alcohol oxidation [27-31]. In the current study, a number of primary and secondary alcohols were converted to the matching aldehydes or ketones in Scheme 1 by using the mediator bromate (BrO_3^-).

2. EXPERIMENTAL SECTION

2.1. Materials and Preparation

In a double-designed beaker-type cell with free air, all reactions were conducted. The chemicals and solvents were acquired from Sigma Aldrich and Fischer Scientific, India Pvt. Ltd. vendors and utilized directly for electrolysis operations. From Biotech Electrophoresis Pvt. Ltd. Yercaud, Tamilnadu, India, a specially built high voltage, aplab power source with 0-60 Volt and 0-3 ampere was purchased. Thin-layer chromatography employing Merck TLC silica gel was utilized to closely monitor the continuous electrolysis processes, and 0.25 mm precoated aluminum sheets were employed to spot the reaction mixtures. By using $KMnO_4$ or a UV lamp, the reaction sites on the pre-coated plates may be seen. Eluents for column chromatography included n-hexane and ethyl acetate. For column chromatography, silica gel with particle sizes of 100–200 mesh was utilized. The other solvents, such as Tetrahydrofuran, Acetonitrile, Chloroform, Dichloromethane, and Toluene, were bought from Alfa-Aesar and Sigma Aldrich. Using a magnetic stirrer, electrolytic chamber reactions were conducted under temperature control. De-ionized water was used to prepare each aqueous solution. Authentic samples of benzaldehyde were used, and ^1H NMR, UV, and FTIR [Bruker-400 MHz] were used to confirm the product in order to compare and calculate the peak area of the experimental products for yield computation. The spectroscopic characteristics matched those that had previously been written about in the literature [32,33].

A solution of sodium bromate mediator (10 mmol) diluted in 80 ml of water was added to a 120 ml undivided beaker-type cell, and a solution of benzyl alcohol (1.02 g, 10 mmol) and chloroform (20 ml) was added to a single compartment electrolytic cell. Sulphuric acid and potassium iodate are present in the upper aqueous layer to maintain the medium's acidity, and benzyl alcohol is present in the bottom organic phase to increase conductivity. The aqueous phase was then injected with two platinum electrodes (each with a 15 cm^2 surface area) until they were barely in contact with the organic phase. The electrodes were spaced 2 cm apart consistently. The magnetic stirring was set to 60 rpm to maintain the biphasic separation between the aqueous and organic phases. At room temperature and a current density of 50 mA/cm^2, galvanic electrolysis was performed statically. After reaching 5 F charges per mole of benzyl alcohol, the stirring was stopped. The product was separated from the lower organic phase using a separating funnel. After drying over anhydrous sodium sulphate and removing the solvent by distilling the residue, the combined organic phase was washed twice with chloroform (2×25ml). This confirmed the existence of 97% benzaldehyde. By designing and modifying the electrolysis parameters, high yields of the desired products were achieved. Every yield is a single [34].

2.2. Standard operating procedure for the biphasic production of aldehydes

All of the chemicals and solvents used (Merck) were of analytical grade. An Aplab power supply served as the electrolysis' direct current source. Deionized water was used to create the electrolyte. Two 15 cm^2 platinum sheets were used as the anode and cathode in a 120 ml undivided glass electrolysis cell with a magnetic stirrer. Using a SHIMADZU LC-8 A column (250 mm 4.6 mm) as the stationary phase, the reaction was observed using HPLC. Chloroform and water (20:80) in a 1 ml/min flow made up the eluent. In order to examine the samples, a UV detector with a 254 nm wavelength was employed. Authentic benzaldehyde samples were used, along with ^{1}H and ^{13}C spectroscopies, to compare and calculate the peak area of the experimental products for yield computation.

2.3. Characterization Techniques

HPLC was used as the stationary phase, with a SHIMADZU LC-8A pump (250 mm × 4.6 mm) serving as the mobile phase. The eluent was composed of water and acetonitrile (80:20). The flow was kept at 1 mL per minute.

Using a UV detector, samples were examined at a wavelength of 254 nm.

NMR spectroscopy: On a 400 MHz spectrometer, the ^{1}H and ^{13}C NMR spectra were captured. Values for chemical shifts are expressed as values. ^{1}H NMR is used to reference internal standards relative to Me_4Si (0.0 ppm), while ^{13}C NMR is used to assess standards relative to $CDCl_3$ (77.16 ppm). The following acronyms were used for NMR: s-singlet; t-triplet; q-quadruplet; dd-doublet of doublet.

Fourier-Transform Infra-Red Spectroscopy: Using KBr pellets, FT-IR spectra were captured on a Perkin-Elmer 100 Spectrochem series.

Without additional purification, reagents were employed that were purchased commercially. Every experiment was carried out in a free-air environment in a beaker-style electrolysis cell. 1 µL of the aliquot was periodically taken and injected into HPLC that was loaded with an (acetonitrile: water) ratio to monitor the reactions. A detector for ultraviolet light (243 nm) was utilized. The sample flow rate was set at 0.2 mL/min. A Bruker (400 MHz) spectrometer was used to record the ^{1}H and ^{13}C NMR spectra. With reference to the solvent peak, the chemical shift and the chloroform used as a reference solvent for ^{1}H NMR (7.26 ppm) are reported in ppm. Using $CDCl_3$, chemical shifts in the ^{13}C NMR spectra were measured

(77.23 ppm). All of the solvents CH_2Cl_2, and $CHCl_3$ were dried and distilled in accordance with standard methods before the studies began.

3. RESULTS AND DISCUSSION

3.1. Electrochemical bromate-mediated oxidation of benzyl alcohol

In practical electro-organic synthesis, two-phase electrolysis offers a clear advantage over homogeneous and emulsion electrolysis. Lower selectivity is shown inhomogeneous systems as a result of excessive substrate oxidation on the electrode surface, which produces a variety of products. Electrode passivation causes a high current density and high energy consumption in emulsion electrolysis. The expended mediator may be difficult to separate in the first two methods mentioned. In systems with two phases of electrolysis, the reactive species created by the electrolytic oxidation of a mediator in the aqueous phase selectively react with the substrate to produce the products in the interphasic space between the organic and aqueous phases. After the electrolysis is finished, the product is obtained by doing a routine workup on the organic layer. The following parameters were examined, and the findings are presented, during the two-phase electrolysis process used to selectively oxidize benzyl alcohol.

3.2. Impact of charge passed

The highest current efficiency (97%) was achieved when 5 F of electricity was passed, which caused 97% of the benzyl alcohol to be selectively converted to benzaldehyde. Even when the electrolysis was conducted with a higher charge than was necessary, the yield did not significantly rise; only the time duration did. When 3 F of electricity was used to oxidation of benzyl alcohol to benzaldehyde, the current efficiency dramatically decreased (Table 1) despite the fact that the product yield was hardly affected.

Table 1. Effect of charge passed

S. No	Charge Passed (F/mol)	Benzaldehyde Yield (%)	Current Efficiency (%)
1	2	72	72
2	3	83	83
3	4	94	94
4	**5**	**97**	**97**

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.3. Impact of current density

In order to conduct the reactions, 5 F of electricity was passed at various current densities ranging from 30 to 70 mA cm^{-2} (Table 2). The benzyl alcohol oxidation process is time-consuming at low current densities. When the reaction progressed to its final stage at higher current densities than it did at its beginning, cell voltage increased. It illustrates how current efficiency and the production of benzaldehyde have both declined. The optimal current density, thus, for the selective oxidation of benzyl alcohol is 50 mA cm^{-2}.

Table 2. Effect of current density

S. No	Current density (F/mol)	Benzaldehyde Yield (%)	Current Efficiency (%)
1	30	74	74
2	40	85	85
3	**50**	**97**	**97**
4	60	92	92
5	70	89	89

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.4. Impact of acid

Another important factor in redox-mediated oxidations, particularly at greater densities is the presence of acids. Studies were done to see how acids affected the way benzyl alcohol was oxidized. With a variety of acid media, including H_2SO_4, HNO_3, and $HClO_4$, two-phase electrolysis was performed.

Table 3. Effect of acid

S. No	Acids	Benzaldehyde Yield (%)	Current Efficiency (%)
1	H_2SO_4	92	92
2	HNO_3	89	89
3	$HClO_4$	74	74
4	**HCl**	**97**	**97**

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2. Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase. Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

All other acids were shown to operate similarly well, but HCl was picked because of its low price. To determine how acid concentration affected the selective oxidation of benzyl alcohol, additional investigations were carried out. With higher HCl concentrations, the production of benzaldehyde did not rise. It was found that using a lower acid concentration of roughly 0.37 M HCl favored the selective oxidation of benzyl alcohol. In order to increase conductivity, the acid may be utilized as a supporting electrolyte.

3.5. Impact of acid concentration

Indirect electrochemical oxidation of benzyl alcohol was performed using various concentrations of HCl. Details of the experiments are provided in Table 4. It was found that the maximum yield of benzaldehyde (97%) was obtained when 18 mmol concentration of hydrochloric acid was used. However, since using less acid always promotes green chemistry, we chose to use 8.5 mmol of acid as the optimal condition.

Table 4. Effect of acid concentration

S. No	Acid concentration	Benzaldehyde Yield (%)	Current Efficiency (%)
1	**8.5**	**97**	**97**
2	10.4	82	82
3	13.6	73	73
4	16.2	65	65
5	19.8	50	50

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.6. Impact of solvent

The yield of benzaldehyde (97%) from carbon tetrachloride, one of the solvents utilized for the selective oxidation of benzyl alcohol, was slightly greater than that of the other solvents (Table 5).

Table 5. Effect of solvent

S. No	Solvents	Benzaldehyde Yield (%)	Current Efficiency (%)
1	CH_3CN	77	77
2	CH_2Cl_2	84	84
3	CCl_4	88	88
4	**$CHCl_3$**	**97**	**97**

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

Due to the cost and negative environmental effects, it was abandoned. Similar to how acetonitrile, which is miscible with water, creates a homogeneous phase with the electrolyte, raising the cell voltage (to 3.5 V) and ultimately increasing energy consumption, which creates issues when trying to separate the used mediator for recycling. The two-phase electrolysis was therefore best performed using chloroform.

3.7. Impact of bromate mediator concentration

In an undivided beaker-type cell, benzyl alcohol was selectively oxidized using sodium bromate as the mediator at 30-33 °C. No change was seen in the yield of benzaldehyde as the bromate concentration rose from 0.63 to 2.3%. It demonstrates that the generation of bromate radical species only requires a mediator concentration of 0.63%. For the rapid and selective oxidation of benzyl alcohol, this radical species immediately reacted at the interface between the organic and aqueous phases. Finally, the mediator failed to encourage further oxidation of the product benzaldehyde.

Table 6. Effect of bromate mediator concentration

S. No	Bromate mediator concentration	Benzaldehyde Yield (%)	Current Efficiency (%)
1	14.2	64	64
2	9.5	76	76
3	6.4	79	79
4	3.8	85	85
5	**0.63**	**97**	**97**

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.8. Impact of agitation

Effect of agitation on the electrochemical oxidation of benzyl alcohol in the biphasic medium was the next parameter used for the study. It was examined under ideal experimental conditions at rpms ranging from 30 to 70. Table 7 provides specifics on the tests that were carried out. It was found that 60 rpm was the best stirring speed for oxidizing benzyl alcohol, with a yield of 97%. Additionally, it was discovered that biphase continuity was advantageous at this rpm. Although there were two phases present at lower rpm as separate layers, electrolytically produced species had to move from the aqueous phase to the organic phase relatively far in order to attack the substrate. The yield of benzaldehyde remained constant when the agitation rate was raised over 60 rpm.

Table 7. Effect of agitation

S. No	Agitation	Benzaldehyde Yield (%)	Current Efficiency (%)
1	30	82	82
2	40	80	80
3	50	86	86
4	**60**	**97**	**97**
5	70	84	84

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.9. Impact of Temperature

At various temperatures, biphasic medium electrolysis was used to study the oxidation of benzaldehyde oxime. Table 8 provides specifics on the tests that were carried out. The output of benzaldehyde increased as the temperature rose from 30 to 40 °C [35]. Temperature increases between 40 and 60 °C did not promote oxidation. At this temperature, the organic solvent was seen to evaporate. At 35 °C (97%), the benzaldehyde output was at its highest.

Table 8. Effect of temperature

S. No	Temperature	Benzaldehyde Yield (%)	Current Efficiency (%)
1	20-30°C	67	67
2	**30-40°C**	**97**	**97**
3	40-50°C	70	70

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.10. Impact of various electrode materials

In the two-phase electrolysis method for selective benzyl alcohol oxidation, the electrode pairs used are listed in Table 9 in various varieties. Electrolysis experiments were conducted using electrode materials made of SS/SS, C/C, C/SS, SS/C and Pt/Pt. It was discovered that all five electrode pairings exhibit almost the same efficiency [36]. Electrodes made of platinum/platinum were favored from a practical standpoint due to their widespread availability and affordable price.

Table 9. Effect of various electrode materials

S. No	Various electrodes	Benzaldehyde Yield (%)	Current Efficiency (%)
1	SS/SS	85	85
2	C/C	89	89
3	C/SS	91	91
4	SS/C	92	92
5	**Pt/Pt**	**97**	**97**

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

3.11. Impact of reusability of Sodium bromate mediator

Phase separation was used to separate the aqueous and organic phases of the sodium bromate produced by electrochemical oxidation.

Table 10. Effect of reusability of sodium bromate mediator

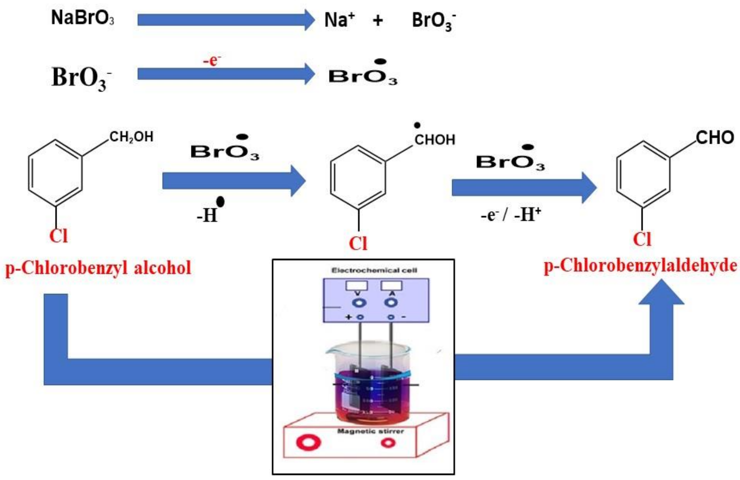
S. No	Reproducibility factor time	Benzaldehyde Yield (%)	Current Efficiency (%)
1	**1**	**97**	**97**
2	2	95	95
3	3	90	90
4	4	89	89

Reaction circumstance: Platinum anode and cathode (area: 15 cm^2), current density: 50 mA/cm^2; Charged passed: 6 F/mol Chloroform (20 ml) and benzyl alcohol (2 ml) in the organic phase; Aqueous phase: 80 ml of deionized water with 10 mmol $NaBrO_3$ and 8.5 mmol, 60 rpm for stirring

The combined organic extract was then processed as usual to produce benzaldehyde from the combined organic extract. For the oxidation of benzyl alcohol, the isolated aqueous phase was recycled three times. The findings are shown in Table 10. It demonstrates that the yield of benzaldehyde consistently decreases, most likely as a result of handling the loss of sodium bromate mediator during subsequent tests. In each of the subsequent tests, an additional 10% sodium bromate was administered to refill the sodium bromate concentration, while benzaldehyde remained constant at 97%.

3.12. Proposed Electrochemical Oxidation Mechanism

For the current inquiry, a potential response mechanism is put forth (Scheme 2). The creation of the bromate radical as an intermediate result from the one-electron transfer that takes place while the reaction develops in the aqueous phase. The unstable persulfate radical produced in situ combines with the substrate in the organic phase to produce benzylic radical species after quickly oxidizing the alcohols in the interfacial region. Following cleavage, this benzylic radical species produces the desired result [37-39].



Scheme 2. Mechanism of electrochemical oxidation of substituted benzyl alcohol

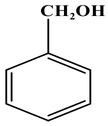
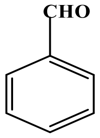
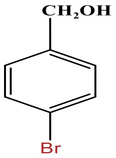
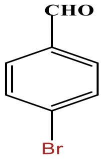
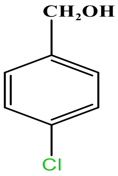
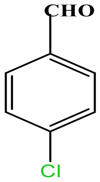
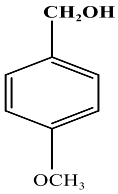
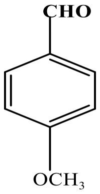
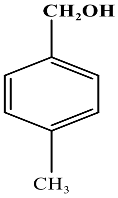
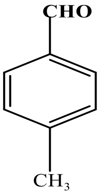
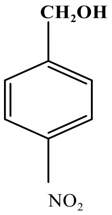
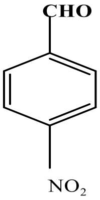
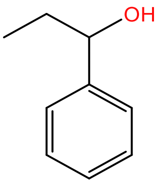
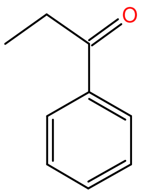
3.12. Impact of alcohol substitutes

In order to assess the generality of the reaction, various alkyl aromatic alcohols were investigated under optimal conditions. The results are presented in Table 11. An excellent product (97%) was produced by the electrochemical oxidation of benzyl alcohol in a biphasic system with a charge density of 6 F/mol. This biphasic process oxidized substituted alcohols to corresponding carbonyl compounds in high yields in a single compartment call. Table 11 shows the yields of the main commodities. Under optimal reaction conditions, benzoyl alcohol (entry 1) underwent smooth oxidation, yielding only the required aldehyde and no further oxidation to acids.

An excellent product (97%) was produced by the electrochemical oxidation of benzyl alcohol in a biphasic system with a charge density of 5F/mol. This biphasic process oxidized substituted alcohols to corresponding carbonyl compounds in high yields in a single compartment call.

The yields of the various commodities are displayed in Table 11. Benzyl alcohol (entry 1) was smoothly oxidized under ideal reaction circumstances to produce only the necessary aldehyde, with no extra oxidation to acids. The -I action of the halogen group made it necessary to require 6 F/mol of electricity to substitute alcohols with electron-withdrawing groups, such as p-Bromo benzyl alcohol (entry 2), p-chlorobenzyl alcohol (entry 3) and which had maximum yields of 88% and 84%, respectively.

Table 11. Effect of alcohol substitutes

Entry	Substrate	Charge Passed (F/Mol)	Product	Yield (%)	Current Efficiency (%)
1		5		97	97
2		5		88	88
3		5		84	84
4		5		85	85
5		5		82	82
6		5		12	6
7		5		45	45

The oxidation of aromatic alcohol substituted with an electron-donating group, such as methoxy and the methyl group (entries 4,5) was attributed to the steric impact of the CH_3-

group attached in the para position of the aromatic moiety, generating 85% and 82% with 5 F/mol current.

Due to the significant instability of the carbocation intermediate that would be produced during the reaction, the reaction only advanced 12% in the case of benzyl alcohol replaced by the extremely electron-withdrawing nitro group (entry 6). Additionally, there was insufficient solubility of the nitro compound in chloroform. Due to the weak solubility of the strong electron-withdrawing group, such as the nitro substituted benzyl alcohol (entry 6), in chloroform solvent, only 12% of the expected amount of aldehyde was produced, and the reaction did not proceed as expected due to the high degree of carbocation intermediate destabilization.

In comparison to primary alcohols, secondary alcohols like 1-phenylpropanol (entry 7) required a somewhat longer reaction time to give the equivalent ketone in 45% yield. This is to be expected as the additional methyl group may have sterically prevented the large iodate radical from approaching the benzylic hydrogen, resulting in a low yield.

4. CONCLUSION

For the purpose of selective oxidation of different benzyl alcohol derivatives, we have created a highly effective electrochemical synthesis. This is the first study to successfully change alcohols without using harmful metals, instead making optimal use of electricity using sodium bromate as a mediator. This straightforward ecologically friendly method makes related alcohol scaffolds freely accessible. Here, various functional groups are described. This flawless electro-organic synthesis was carried out in a biphasic setup cell using non-toxic electrodes like platinum. The current process uses a redox mediator to oxidize primary and secondary alcohols, producing the corresponding aldehydes or ketones with moderate to high product yields. It is significant to note that primary alcohols are oxidized to the corresponding aldehydes and that overoxidation to the corresponding carboxylic acid does not occur. Also, it provides advantages such as a catalyst that is devoid of metal, no secondary products, high yield, and catalytic mediator recycling. The entire procedure is therefore entirely sustainable and acceptable to the environment.

Declarations of interest

The authors declare no conflict of interest in this reported work.

REFERENCES

[1] M. Passiniemi, A.M. Koskinen, and Beilstein, J. Org. Chem. 9 (2013) 2641.

[2] G.J. Ten Brink, I.W.C.E. Arends, and R. A. Sheldon, Science 287 (2000) 1636.

[3] H.Y. Shen, L.Y. Ying, H.L Jiangand, Z.M.A. Judeh, Int. J. Mol Sci. 6 (2007) 505.

[4] T. Raju, S. Manivasagan, B. Revathy, K. Kulangiappar, and A. Muthukumaran, Tetrahedron Lett. 48 (2007) 3681.

[5] C. Christopher, S. Lawrence, M.A. Kulandainathan, K. Kulanjiappar, M.E. Raja, N. Xavier, and S. Raja, Tetrahedron Lett. 53 (2012) 2802.

[6] T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, and Y. Ishii, J. Org. Chem. 65 (2000) 6502.

[7] I. Mohammad poor-Baltork, Molecules 6 (2001) 900.

[8] Y. Kwon, C. S. Stanley Lai, P. Rodriguez, and T.M. Marc-Koper, J. Am. Chem. Soc.,133 (2011) 6914.

[9] A. Kwast, K. Stachowska, A. Trawczyński, and Z. Wróbel, Tetrahedron Lett. 52 (2011) 6484.

[10] H.J. Park, and J.C. Lee, Synlett. 1 (2009) 79.

[11] M. Yan, Y. Kawamata, and P.S. Baran, Chem. Rev. 117 (2017) 13230.

[12] G.S. Mohle, E. Rodrigo, M. Zirbes, S.R. Waldvogel, Angew. Chem. Int. Ed. 57 (2018) 5594.

[13] S. Herold, S. Mohle, M. Zirbes, F. Richter, H. Nefzger, S.R. Waldvogel, Eur. J. Org. Chem. 7 (2016)1274.

[14] B.A. Frontana-Uribe, R.D. Little, J.G. Ibanez, A. Palma, and R. Vasquez-Medrano, Green Chem. 12 (2010) 2099.

[15] H.J. Schafer, M. Harenbrock, E. Klocke, M. Plate, and A. Weiper-Idelmann, Pure Appl. Chem.79 (2007) 2047.

[16] J. Simonet, and J.F. Pilard, H. Lund, O. Hammerich, M. Dekker, Organic Electrochemistry, ed. New York (2001) pp. 1163.

[17] B. Elsler, A. Wiebe, D. Schollmeyer, K.M. Dyballa, R. Franke, and S.R. Waldvogel, Chem. Eur. J. 21 (2015) 12321.

[18] B. Elsler, D. Schollmeyer, K.M. Dyballa, R. Franke, and S.R. Waldvogel, Angew. Chem. 53 (2014) 5210.

[19] P.W. Raess, M.S. Mubarak, M.A. Ischay, M.P. Foley, T.B. Jennermann, K. Raghavachari, and D.G. Peters, J. Electroanal. Chem. 603 (2007) 124.

[20] N.L. Wolf, D.G. Peters, and M.S. Mubarak, J. Electrochem. Soc. 1 (2006) 153.

[21] E. Steckhan, T. Arns, W.R. Heineman, G. Hilt, D. Hoormann, J. Jorissen, L. Kroner, B. Lewall, and H. Putter, Chemosphere 43 (2001) 63.

[22] H.Y. Chen, H.B. Ji, X.T. Zhou, J.C. Xu, and L.F. Wang, Catal. Commun. 10 (2009) 828.

[23] C. Christopher, S. Lawrence, A. John Bosco, N. Xavier, and S. Raja, Catal. Sci. Technol. 2 (2012) 824.

[24] T. Raju, S. Manivasagan, B. Revathy, K. Kulanjiappar, and A. Muthukumaran, Tetrahedron Lett. 48 (2007) 3681.

[25] T. Raju, K. Kulangiappar, M. Anbukulandainathan, and A. Muthukumaran, Tetrahedron

Lett. 46 (2005) 7047.
[26] A.V. Biradar, M.K. Dongare, S.B. Umbarkar, Tetrahedron Lett. 50 (2009) 2885.
[27] S. Zhang, L. Xu, and M.L. Trudell, Synthesis 11 (2005) 1757.
[28] G. An, M. Lim, K.S. Chun, and H. Rhee, Synlett. 3 (2007) 95.
[29] S. Maignien, S. Ait-Mohand, and J. Muzart, Synlett. (1996) 439.
[30] S. Velusamy, and T. Punniyamurthy, Org. Lett. 6 (2004) 217.
[31] M. Musawir, N. Paul Davey, G. Kelly, and I.V. Kozhevnikov, Chem. Commun. 1 (2003) 1414.
[32] A. John Bosco, S. Lawrence, C. Christopher, S. Radhakrishnan, A.A.J. Rosario, S. Raja, and D. Vasudevan, J. Phys. Org. Chem. 28 (2015) 591.
[33] R. Jagatheesan, K. Joseph Santhana Raj, S. Lawrence, and C. Christopher, RSC Advances 6 (2016) 35602.
[34] A. ViniPriya, J. Bosco, T. Maiyalagan, N. Xavier, and D. Vasudevan, Int. J. Electrochem. Sci. 12 (2017) 1272.
[35] T. Torii, S. Inokuchi, T. Matsumoto, Saeki, and T. Oki, Bull. Chem. Soc. Jpn. 63 (1990) 852.
[36] A. Vinipriya, A. JohnBosco, T. Maiyalagan, N. Xavier, and D. Vasudevan, Int. J. Electrochem. Sci. 12 (2017) 1272.
[37] H.Y. Chen, H.B. Ji, X.T. Zhou, J.C. Xu, and L.F. Wang, Catal. Commun. 10 (2009) 828-832.
[38] A.J. Bosco, S. Lawrence, C. Christopher, S. Radhakrishnan, A.A. Joseph Rosario, S. Raja, and D. Vasudevan, J. Phys. Org. Chem. 28 (2015) 591.
[39] R. Jagatheesan, K.J.S. Raj, S. Lawrence, and C. Christopher, RSC Advances 6 (2016) 35602.