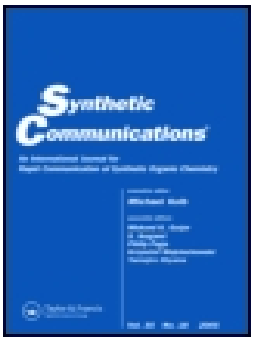

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An expeditious and efficient method for the oxidation of benzyl alcohols by homogeneous electrolysis

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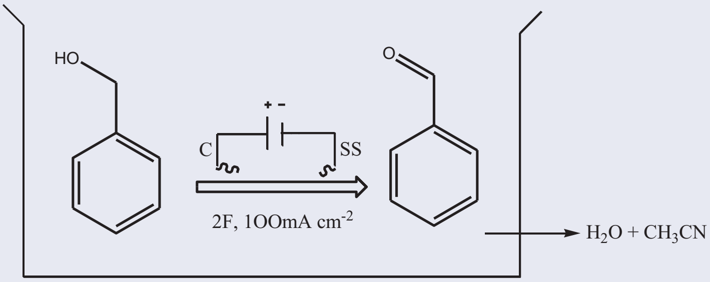
ABSTRACT

A greener and inexpensive electrochemical method has been developed for the oxidation of benzyl alcohols by homogeneous electrolysis. The electrochemical reaction was carried out in an undivided cell equipped with carbon and stainless steel electrodes at room temperature. The homogeneous solution made up of acetonitrile/water containing substrate and ammonium bromide with a catalytic amount of H_2SO_4 as supporting electrolyte. The reaction condition was optimized with various electrochemical experimental parameters and evaluated with various substituted benzyl alcohols to result in excellent yield of aldehydes (>83%).

GRAPHICAL ABSTRACT



Electrochemical oxidation of benzyl alcohol to benzaldehyde

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KEYWORDS
Ammonium bromide; benzaldehyde; benzyl alcohol; electrochemical oxidation; homogeneous electrolysis; undivided cell

Introduction

Since the corresponding carbonyl compounds can be used as important and versatile precursors for the synthesis of fine chemicals such as fragrances, pharmaceutical intermediates and beverage or food additives, the selective oxidation of alkyl aromatics to corresponding carbonyl compounds is one of the most significant reactions in laboratory and industrial synthetic organic chemistry.[1–7] Oxidation of organic substrate in the absence of oxidizing agent is an important transformation in synthetic organic

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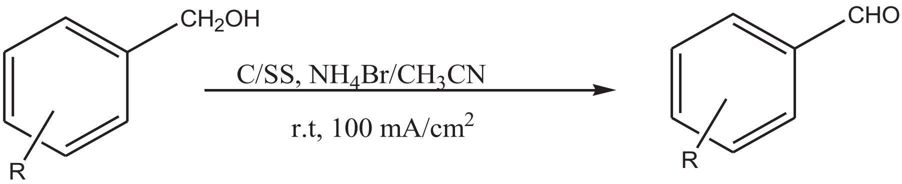


Scheme 1. Homogeneous electrolysis of benzyl alcohol to benzaldehydes.

chemistry. This subject is intensively investigated and achieved by electrochemical method in the present study.

Generally electrochemical oxidation is carried out using transition metal compounds such as ruthenium (VIII) oxide, chromium (VI) oxide, permanganates and dichromates to bring about these transformations. Most of these reagents are toxic, expensive and also generates environmental wastes.[8–17] Moreover, electrochemical method has numerous remarkable advantages like an ecofriendly process, short reaction time, simple electrochemical cell set up, easy-control condition and economically cheap reagents compared with the conventional reactions.[18,19] Further, the existing electrochemical methods for the conversion of alcohol to aldehydes is carried out by biphasic system which demands mediators[20,21] and harmful acid like HBr.[22] In continuation of our previous work,[23] herein we examined and report a simple method for the preparation of arylaldehydes from its respective benzyl alcohols by homogeneous electrolysis at ambient temperature as shown in Scheme 1.

In this electrolysis reaction, benzyl alcohols as substrates, aqueous ammonium bromide salt, supporting electrolyte and minimum amount of organic solvent are the required substances. No additional substances such as catalyst, mediators, oxidants, or ligands are necessary to achieve effective electrochemical oxidation.

Results and discussion

Eletrochemical oxidation of benzyl alcohol

In two-phase electrolysis, mediator is required to bring the product conversion. Similarly, in emulsion electrolysis, electrode passivation occurs. Conversely, homogenous electrolysis has a discrete advantage over the above two methods by providing adequate contact for generated transient hypobromous acid with reactant. Hypobromous acid is an unstable substance and is therefore prepared in situ by electrolysis. In the selective oxidation of benzyl alcohol by homogenous electrolysis, the following optimization studies were carried out to afford the excellent yield and the results are reported. Further, the optimized homogeneous constant current electrolysis system is applied for the oxidation of substituted benzylic alcohols to the corresponding aldehydes at room temperature in an undivided cell.

Effect of current density

The reactions were carried out at different current densities from 30 to 100 mA cm^{-2} by passing 2 F of electricity. The maximum yield and current efficiency was achieved at

100 mA cm^{-2} (Table 1). Furthermore, it takes very short time to carry out the electrolysis. Hence, this higher current density (100 mA cm^{-2}) was elected as an optimum current density for further optimization studies.

Effect of charge passed

To afford good yield in short reaction time, 100 mA cm^{-2} was chosen and the electrolysis was carried out by applying various charges from 2.0 to 4.0F. The maximum yield is reached with high current efficiency at a charge of 2.0F/mole. There are no remarkable changes in the product yield even after passing upto 4.0F/mole as shown in Table 2.

Effect of temperature

Table 3 shows the effect of temperature on the electrochemical conversion of benzyl alcohol. There is an increase in benzaldehyde yield with decrease of temperature from 50 to 30 °C. It clearly indicates about the good stability of hypobromous acid at room temperature. Hence, 30 °C was preferred as optimum temperature for this electrolysis reaction.

Effect of bromide salt

In order to achieve the electrochemical oxidation of benzyl alcohol by using simple and cheaper salt, the effect of various bromide salts as KBr, NaBr and NH_4Br was investigated (Table 4).

Table 1. Simple salt mediated electrochemical oxidation of benzyl alcohol*.

S. No.	Current density (mA cm^{-2})	Benzaldehyde yield (%)	Current efficiency (%)
1	30	81	81
2	50	81	81
3	70	82	82
4	100	83	83

*Reaction mixture and conditions: 60% NH_4Br + 0.3 M H_2SO_4 + 10 mmol benzyl alcohol + water 80% – acetonitrile 20%. Charge passed, 2 F; Electrodes, C/SS, Temperature, 30°C, undivided cell.

Table 2. Effect of charge passed on the electrochemical oxidation of benzyl alcohol by homogeneous electrolysis*.

S. No.	Charge passed (F)	Benzaldehyde yield (%)	Current efficiency (%)
1	2	83	83
2	3	84	56
3	4	85	43

*Reaction mixture and conditions: 60% NH_4Br + 0.3 M H_2SO_4 + 10 mmol benzyl alcohol + water 80% – acetonitrile 20%. Current density, 100 mA cm^{-2}; electrodes, C/SS, temperature, 30°C, undivided cell.

Table 3. Effect of temperature on selective oxidation of benzyl alcohol*.

S. No.	Temperature (°C)	Benzaldehyde yield (%)	Current efficiency (%)
1	50	45	45
2	40	56	56
3	30	83	83
4	20	60	60
5	10	10	10

*Reaction mixture and conditions: 60% NH_4Br + 0.3 M H_2SO_4 + 10 mmol benzyl alcohol + water 80% – acetonitrile 20%. Current density, 100 mA cm^{-2}; charge passed, 2 F; electrodes, C/SS, undivided cell.

Table 4. Effect of halide salt variation on oxidation of benzyl alcohol*.

S. No.	Bromide salt	Benzaldehyde yield (%)	Current efficiency (%)
1	KBr	78	78
2	NaBr	80	80
3	NH_4Br	83	83

*Reaction mixture and conditions: 60% Bromide salts + 0.3 M H_2SO_4 + 10 mmol benzyl alcohol + water 80% – acetonitrile 20%. Current density, 100 mA cm^{-2}; charge passed, 2 F; electrodes, C/SS, temperature, 30°C, undivided cell.

Table 5. Effect of solvent on electroselective oxidation of benzyl alcohol.

S. No.	Solvent	Benzaldehyde yield (%)	Current efficiency (%)
1	DMSO	76	76
2	CH_3OH	81	81
3	$CHCl_3$**	80	80
4	CH_3CN	83	83

*Reaction mixture and conditions: 60% NH_4Br + 0.3 M H_2SO_4 + 10 mmol benzyl alcohol + water 80% – solvent 20%. Current density, 100 mA cm^{-2}; charge passed, 2 F; electrodes, C/SS, temperature, 30°C, undivided cell. **Biphasic electrolysis.

From the table it was observed that the electrochemical oxidation of benzyl alcohol was effectively achieved when using NH_4Br salt. Further, minimum quantity of NH_4Br is required to prepare saturated solution. Thereby this salt was suggested for this reaction condition.

Effect of acid

To scrutinize the best supporting electrolyte for the present study, the electrochemical conversion of benzyl alcohol to benzaldehyde was carried out in aqueous solution of saturated NH_4Br containing catalytic amount of various supporting electrolytes like HNO_3, HCl, $HClO_4$ and H_2SO_4. All the acids are performed equally well, but H_2SO_4 was preferred as good supporting electrolyte due to its low cost, availability and higher conductivity (<2 V).

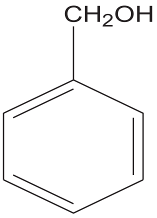
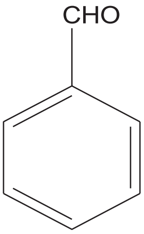
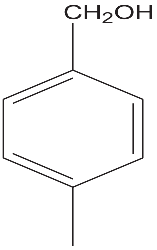
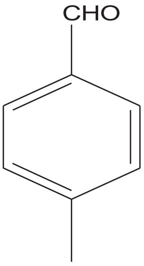
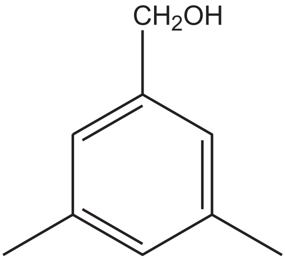
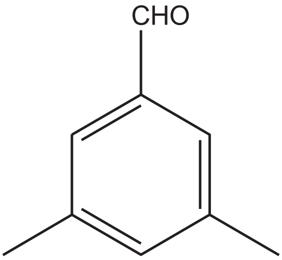
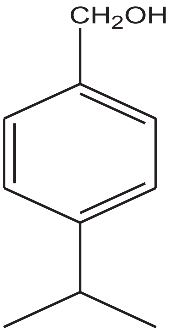
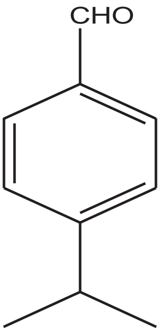
Effect of solvent

Concerning the influence of solvent, the electrolysis was attempted with different solvents like DMSO, CH_3OH, $CHCl_3$ and CH_3CN at room temperature (Table 5). Among these solvents CH_3CN performed well at 2 F/mole and was suggested as a suitable solvent for the present optimization study.

Reusability of spent aqueous bromide salt solution

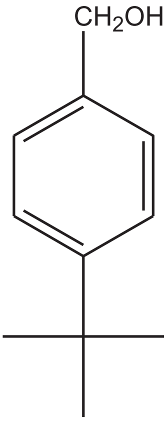
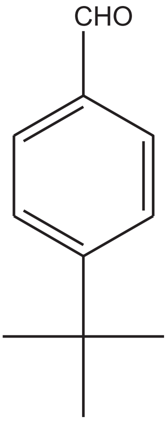
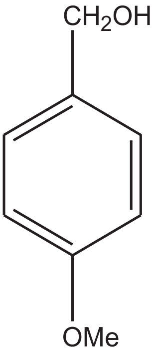
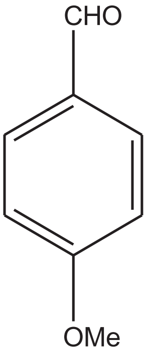
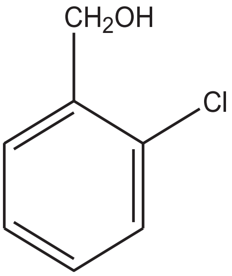
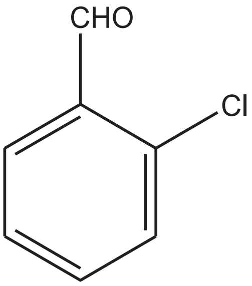
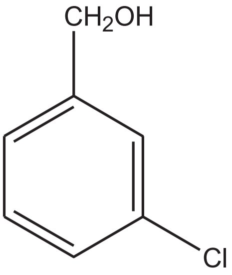
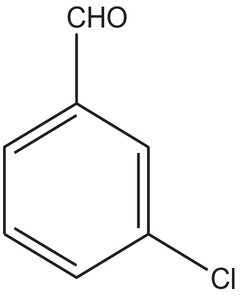
After the completion of homogeneous electrolysis, benzaldehyde and unreacted benzyl alcohol was separated using appropriate solvents from the reaction mixture containing aqueous salt solution. Thereby the remaining aqueous salt solution was available for further electrolysis reaction. The yield was obtained as 65, 52, and 38% in first, second and third reuse, respectively. From the result, it states that the amount of yield was decreased in every further reuse of the bromide salt solution. It indicates the availability of bromide source was less in every successive reuse.

Table 6. Electrochemical oxidation of alcohols by homogeneous electrolysis system*.

Entry	Substrate	Product	Yield (%)	Current efficiency (%)
1.			83	83
2.			80	80
3.			79	79
4.			79	79

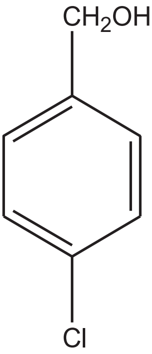
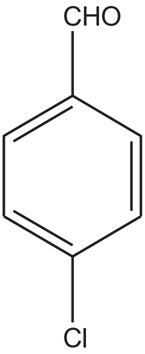
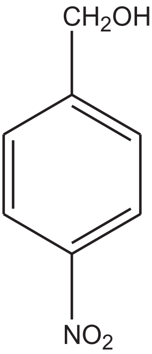
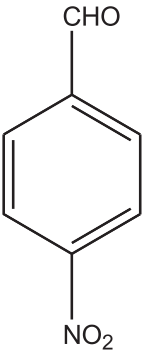
(*continued*)

Table 6. Continued.

Entry	Substrate	Product	Yield (%)	Current efficiency (%)
5.			83	83
6.			80	80
7.			68	68
8.			74	74

(*continued*)

Table 6. Continued.

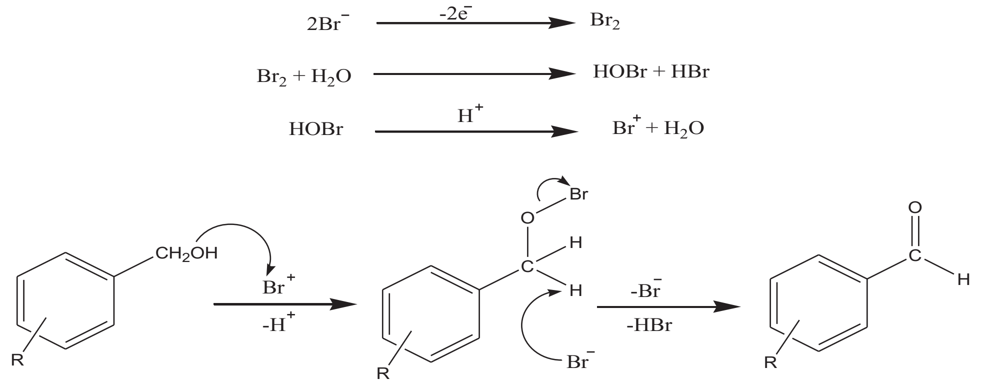
Entry	Substrate	Product	Yield (%)	Current efficiency (%)
9.			78	78
10.			0**	0

*Reaction mixture and conditions: 60% NH_4Br + 0.3 M H_2SO_4 + 10 mmol benzyl alcohol + water 80% – acetonitrile 20%. Current density, 100 mA cm^{-2}; charge passed, 2F; electrodes, C/SS, Temperature, 30°C, undivided cell. **Stirring extended up to 5 hours after electrolysis.

Evaluation of optimized electrolysis condition with substituted benzyl alcohols

To evaluate the scope of this optimized condition and to test the generality of this method, a variety of benzyl alcohols were subjected to the homogeneous electrolysis reaction at room temperature in a single compartment and its corresponding results are listed in Table 6. From the results we observed that, effective electrochemical oxidation occurred at benzyl alcohols substituted with electron donating groups (Table 6, entries 2–6) in excellent yields, whereas benzyl alcohols containing electron withdrawing groups (Table 6, entries 7–9) gave moderate yields at lowest charge of 2 F. Surprisingly, benzyl alcohol substituted with highly deactivating group (Table 6, entry 10) did not follow the electrochemical oxidation reaction.

Based on a literature report, a plausible mechanism for the electrochemical oxidation is given in Scheme 2.[24] The electrochemically generated bromine undergoes hydrolysis, giving hypobromous acid (HOBr) and HBr. The hypobromous acid is unstable thus forms transient Br^+ which can subsequently oxidizes the benzyl alcohols to the corresponding aldehydes as shown in Scheme 2.



Scheme 2. Plausible mechanism for electrochemically generated transient bromonium ion mediated oxidation of benzyl alcohols.

Experimental

General experimental procedure

In an undivided cell (beaker type), 10 mmol of benzyl alcohols, 20 ml of acetonitrile, 80 ml of aqueous ammonium bromide solution (60%) containing catalytic amount of H_2SO_4 (0.3 M) was taken. Two electrodes such as carbon (anode) and stainless steel (cathode) of 15 cm^2 area were introduced at a distance of 2 cm^2 into the undivided cell containing homogeneous solution. The electrolysis was conducted by passing 2 F of electricity galvanostatically at a current density of 100 mA cm^{-2}. The temperature of the electrochemical cell contents was maintained between 30–33 °C during the electrolysis to reduce the solvent evaporation. The whole homogeneous solution was stirred constantly throughout the reaction. After passing required charge per mole (2 F), the current supply was stopped and the reaction mixture alone is allowed to stir another 1 hour to complete the reaction. At the end, the reaction mixture was extracted with ethyl acetate (3 × 25 mL) and the combined organic layer was washed with water (20 mL) and dried over anhydrous sodium sulfate. The solvent was removed by distillation.

The electrochemical reaction was monitored by TLC and Shimadzu HPLC with LC-8A column (250 mm ×4.6 mm) as stationary phase. The eluent consisted of acetonitrile/water (80: 20) at a flow rate of 1 mL min^{-1}. Samples were analyzed at a wavelength of 254 nm with a UV detector coupled to a printer. Authentic samples of benzaldehyde are used to calculate the peak area of the corresponding experimental product for yield calculation.

Conclusion

On electrolysis aqueous ammonium bromide provides bromonium ion for the oxidations of benzyl alcohols to its corresponding aldehydes. The advantages of the present method include simple experimental set up, low cost bromide salt, cheaper electrodes, room temperature, in-situ generated transient hypobromous acid, short reaction time, green solvent water used as maximum and no by-product. Further, the reuse of the spent electrolyte solution is the remarkable advantage in this method. The above features also lead to electrochemical regeneration with high current efficiencies at high current densities and rapid oxidation without oxidizing agent.

Supplementary information (experimental procedures, 1H and 13 C NMR spectra, HPLC traces) associated with this article can be found via the "Supplementary Content" section of this article's webpage.

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