A Novel Biphasic Electrolysis Method for the Oxidation of Benzaldoximes Using Potassium Perchlorate as the Mediator

Biju Joy, M. Balaganesh and S. Joseph Selvaraj[*]

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

Abstract

Benzaldehyde oxime can be readily converted to the corresponding benzaldehyde in biphasic medium. The reaction was carried out with platinum electrodes at room temperature in an undivided cell within constant biphasic medium consisting of chloroform containing benzaldehyde oxime and an aqueous solution of potassium perchlorate as a mediator with a catalytic amount of H_2SO_4. The electrochemical oxidation was optimized with various experimental parameters to result in the high yield of benzaldehyde (80%).

Keywords: Undivided cell, selective oxidation, benzaldehyde oxime, potassium perchlorate, biphasic medium, benzaldehyde.

Introduction

Oximes are useful in organic chemistry as protecting groups [1], synthetic intermediates for producing amines [2] and nitriles [3]. They are used for purification and characterization of aldehydes and ketones [4-7]. They act as good intermediates for many reactions such as the preparation of amides by Beckmann rearrangement [8]. Oximes can also be prepared from non-carbonyl compounds. A survey of the literature revealed that a wide range of oxidizing agents have been used for this purpose with different degrees of success. A mild, simple process for the effective deoximation of aldoximes has been reported using Amberlyst-15 [9].

Several metallic and non-metallic deoximation reagents such as tert-butyl hydroperoxide, thallium nitrate, $KMnO_4$/alumina, N-bromosuccinimide, chloranil, ammonium persulfate, periodic acid, tetra-butylammonium tetra-fluoroborate, and metalloporphyrins [10-18] have been used over the years. Biphasic electrolysis has the advantages of better electrical conductivity, current yield, selectivity and better reusability of the mediator [19-21]. Herein we report the conversion of benzaldehyde oximes to benzaldehyde in 80% yield through a biphasic electrolysis using potassium perchlorate mediator.

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[*] Corresponding author. E-mail address: drsjs2014@yahoo.com

Experimental

Materials and analysis

All reagents and solvents used were analytical grade (Merck). An Aplab power source was used as the direct current source for electrolysis. Deionised water was used to prepare the electrolyte. A beaker type glass cell (120 mL capacity) equipped with a magnetic stirrer was used and two platinum sheets each of 15 cm^2 area were used as the electrodes. The reaction was monitored by a Shimadzu HPLC with LC-8A column (250 mm × 4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (60:40) at a flow rate of 1 mL/min. Samples were analysed by UV detector at a wavelength of 254 nm. Authentic samples of benzaldehyde were used to compare and calculate the peak areas of the experimental products for yield calculation. The product obtained was confirmed by ^1H NMR and ^{13}C NMR spectra [Brucker-300 MHz].

Procedure for the synthesis of benzaldehyde oxime

The benzaldehyde oxime was prepared according to a known procedure [22, 23]. A mixture of 3 g (28 mmol) of the benzaldehyde, 3 g (47 mmol) hydroxylamine hydrochloride, 3 g (38 mmol) pyridine, and 15 mL of ethanol were refluxed for 60 minutes in a water bath. The ethanol was removed by distillation and 15 mL of water were added to the cooled residue. It was placed on an ice bath and stirred until the oxime crystalized. After cooling to room temperature the precipitate was filtered. The residue was dissolved in CH_2Cl_2, washed with water, and extracted into CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness under reduced pressure. The corresponding oxime was obtained in 98% yield.

Electrochemical oxidation of benzaldehyde oxime

A solution of benzaldehyde oxime (1.0 g, 10 mmol) in chloroform (25 mL) was taken in a single compartment cell. To the solution, 90 mL of potassium perchlorate (3.0 g, 21.6 mmol) containing 1.0 g (10.2 mmol) sulphuric acid were added. The aqueous upper layer contains the perchlorate as a mediator and sulphuric acid to maintain the medium acidic and for conductivity purpose. The benzaldehyde oxime was present in the lower organic phase. Then two platinum electrodes (each of 15 cm^2 area) were introduced into the aqueous phase till they just touch the organic phase. The inter electrode distance was maintained at 2 cm. The magnetic stirring was kept at a rate of 60 rpm to keep the aqueous and organic phases in biphasic medium. The electrolysis was conducted galvanostatically at a current density of 50 mA cm^{-2} while maintaining the temperature at 30 - 40 ℃. After passing 6 F charges per mole of benzaldehyde oxime, the stirring was stopped. The lower organic layer containing the product was separated by a separating funnel. The upper aqueous layer was washed twice with chloroform (2 x 25 mL) and the combined organic phase washed with water (2 × 25 mL) and dried over anhydrous sodium sulphate. The solvent was removed by distillation. HPLC analysis of the residue indicated the presence of

80% benzaldehyde. The product was isolated by column chromatography and characterized by ^{1}H NMR and ^{13}C NMR.

Benzaldehyde oxime
^{1}H NMR (300 MHz, CDCl$_3$), δ: 9.06 (1H, s)(N=C–H), 8.17 (1H, s)(O–H), 7.24-7.98 (5H, m).
^{13}C NMR (300 MHz, CDCl$_3$), δ: 150.39 (1C, C=N), 131.79-127.03 (6C, Aromatic carbon).

Benzaldehyde
^{1}H NMR (300 MHz, CDCl$_3$), δ: 10.02 (1H, s)(O=C–H), 7.27-7.90 (5H, m).
^{13}C NMR (300 MHz, CDCl$_3$), δ: 192.35 (1C, H–C=O), 136.83-128.39 (6C, Aromatic carbon).

Results and discussion

The following parameters were studied for the electrochemical oxidation of benzaldehyde oxime. The results are shown in detail in the tables given under each of the parameters.

Table 1. Influence of passed charge.

S.No.	Passed charge(F/mol)	Benzaldehyde yield (%)	Current efficiency (%)
1	2	59	59
2	3	68	46
3	4	72	36
4	5	75	31
5	**6**	**80**	**26**
Experimental conditions			
Passed charge: 2 - 6 F/mol	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Aqueous phase	21.6 mmol KClO$_4$ + 10.2 mmol H$_2$SO$_4$ in 90 mL deionised water	
	Current density	50 mA cm^{-2}	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ℃	
	Stirring rate	60 rpm	

Effect of passed charge

Benzaldehyde oxime was oxidized electrochemically in perchlorate medium (using potassium perchlorate) at different charges ranging from 2 - 8 F. It was carried out in an undivided cell at the optimum experimental conditions. At 2 F the yield of the product was 59% and it increased to 80% at 6 F. The details of the experiments conducted are given in Table 1. It was observed that there wasn't much improvement in the product yield after 6 F. So, 6 F of charge/mole is taken as optimal charge for the oxidation of benzaldehyde oxime.

Effect of current density

Indirect electrochemical oxidation of benzaldehyde oxime was carried out in a single compartment cell at optimum experimental conditions. The current density was varied from 20 - 60 mA cm^{-2}. The details of the experiments conducted are given in Table 2. It was found that the optimum current density for the electrochemical oxidation of benzaldehyde oxime is at 50 mA cm^{-2}, where it produced a result of 80% product yield, as mentioned in the Table 2.

Table 2. Influence of current density.

S.No.	Passed charge (F/mol)	Benzaldehyde yield (%)	Current efficiency (%)
1	20	58	19
2	30	62	21
3	40	71	24
4	**50**	**80**	**26**
5	60	60	20
	Experimental conditions		
Current density: 20 - 60 mA cm^{-2}	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Aqueous phase	21.6 mmol KClO$_4$ + 10.2 mmol H$_2$SO$_4$ in 90 mL deionised water	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

Effect of acids

Different acids like H$_2$SO$_4$, HNO$_3$, HClO$_4$ and HCl were used for the oxidation of benzaldehyde oxime. The details of the experiments conducted are given in Table 3. It was observed that H$_2$SO$_4$ performed well among the acids resulting a maximum yield of 80%. Hence the H$_2$SO$_4$ is chosen as a suitable acid for the indirect electrochemical oxidation of benzaldehyde oxime.

Table 3. Influence of acids.

S.No.	Acid	Benzaldehyde yield (%)	Current efficiency (%)
1	**H$_2$SO$_4$**	**80**	**26**
2	HNO$_3$	61	20
3	HClO$_4$	68	23
4	HCl	50	17
	Experimental conditions		
Aqueous phase:21.6 mmol KClO$_4$ + 10.2 mmol of various acids in 90 mL deionised water	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

Effect of acid concentration

Indirect electrochemical oxidation of benzaldehyde oxime was carried out using different concentrations of H$_2$SO$_4$. The details of the experiments conducted are given in Table 4. It was observed that a maximum yield of benzaldehyde (80%) was obtained when 30.6 mmol concentration of sulphuric acid was used. Though

it is the maximum yield, yet less usage of acid always helps green chemistry, so we chose to use 10.2 mmol acid as the optimal condition, since it gives 80% yield.

Table 4. Influence of acid concentration.

S.No.	Acid concentrations (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	**10.2**	**80**	**26**
2	15.3	82	27
3	20.4	83	28
4	25.5	83	28
5	30.6	85	29
Experimental conditions			
Aqueous phase: 21.6 mmol KClO₄ + 10.2 - 30.6 mmol H₂SO₄ in 90 mL deionised water	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

Effect of potassium perchlorate concentration

Potassium perchlorate was used as a mediator for the selective electrochemical oxidation of benzaldehyde oxime. It was carried out in a beaker-type undivided cell at 30 - 40 °C and the optimum experimental conditions were followed as mentioned in the Table 5. The yield of benzaldehyde increased to 80% with the increase of perchlorate concentration from 7.2 - 21.6 mmol. Further increase of perchlorate concentration did not give much improvement in the selective oxidation of benzaldehyde oxime.

Table 5. Influence of potassium perchlorate concentration.

S.No.	Potassium perchlorate concentrations (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	7.2	66	22
2	10.8	72	24
3	14.4	75	25
4	18.0	78	26
5	**21.6**	**80**	**26**
Experimental conditions			
Aqueous phase: 7.2 - 21.6 mmol KClO₄ + 10.2 mmol H₂SO₄ in 90 mL deionised water	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

Effect of agitation

The next parameter used for the study was the effect of agitation on the electrochemical oxidation. It was studied at different rpm ranging from 20 to 80 at optimum experimental conditions. The details of the experiments conducted are given in Table 6. It was observed that the ideal stirring rate for the oxidation was 60 rpm, resulting in a yield of 80%. In addition, it was found that constant

maintenance of biphase was favorable at this rpm. At lower rpm, though two phases were present as separate layers and when the electrolysis occurs, electrolytically generated species had to travel comparatively a long distance from aqueous phase to organic phase to attack the substrate. When the agitation rate was increased beyond 60 rpm, the yield of benzaldehyde remained similar.

Effect of solvents

Electrochemical oxidation of benzaldehyde oxime was carried out with various solvents. Among the solvents used, chloroform gave a maximum yield of benzaldehyde (80%) as shown in the Table 7. Though the reaction mixture was homogeneous when acetonitrile and methanol was used as solvent, yet current efficiency and product yield were low.

Table 6. Influence of agitation.

S.No.	Agitation (rpm)	Benzaldehyde yield (%)	Current efficiency (%)
1	20	57	19
2	40	62	21
3	**60**	**80**	**26**
4	80	78	26
Experimental conditions			
Stirring rate: 20 - 80 rpm	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Aqueous phase	21.6 mmol $KClO_4$ + 10.2 mmol H_2SO_4 in 90 mL deionised water	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ℃	

Table 7. Influence of solvents.

S.No.	Solvent	Benzaldehyde yield (%)	Current efficiency (%)
1	**CHCl₃** [a]	**80**	**26**
2	CH_2Cl_2 [a]	77	25
3	CH_3CN [b]	31	10
4	CH_3OH [b]	56	19
Experimental conditions			
Organic phase: benzaldehyde oxime (10 mmol) in 25 mL various solvents	Aqueous phase	21.6 mmol $KClO_4$ + 10.2 mmol H_2SO_4 in 90 mL deionised water	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ℃	
	Stirring rate	60 rpm	

[a] *biphase electrolysis*   [b] *homogeneous electrolysis*

Effect of temperature

The oxidation of benzaldehyde oxime through biphasic medium electrolysis was studied at different temperatures. The details of the experiments conducted are given in Table 8. There was an increase in benzaldehyde yield on the increase of temperature from 30 - 40 °C. Further increase of temperature from 40 - 60 °C did not favour the oxidation. The evaporation of organic solvent was observed at this temperature. The yield of benzaldehyde was maximum at 40 °C (80%).

Effect of electrodes
Table 9 shows the effect of various types of anodes and cathodes employed in the electrochemical oxidation of benzaldehyde oxime by biphasic medium electrolysis at optimum experimental condition. From the Table it is observed that the Pt/Pt electrode combination performed well (80% yield) when compared with other electrodes.

Table 8. Influence of temperature.

S.No.	Temperature (ºC)	Benzaldehyde yield (%)	Current efficiency (%)
1	20 – 30	69	23
2	**30 – 40**	**80**	**26**
3	50 - 60	63	21
Experimental conditions			
Temperature: 20 - 30 °C, 30 - 40 °C, 50 - 60 °C	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Aqueous phase	21.6 mmol $KClO_4$ + 10.2 mmol H_2SO_4 in 90 mL deionised water	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Stirring rate	60 rpm	

Table 9. Influence of electrodes.

S.No.	Electrode (Anode/Cathode)	Benzaldehyde yield (%)	Current efficiency (%)
1	**Pt/Pt**	**80**	**26**
2	Pt/SS*	70	23
3	C/C	41	14
4	C/SS*	37	12
Experimental conditions			
Anode/Cathode: Pt/Pt, Pt/SS, C/C, C/SS	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Aqueous phase	21.6 mmol $KClO_4$ + 10.2 mmol H_2SO_4 in 90 mL deionised water	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

*Pt = Platinum; SS = Stainless Steel; C = Graphite

Effect of substrate concentration
Electrochemical oxidation of benzaldehyde oxime to benzaldehyde was carried out at various substrate concentrations from 5 - 20 mmol at optimum experimental condition. The details of the experiments conducted are given in Table 10. It is observed that, 10 mmol concentration of benzaldehyde oxime gave a maximum yield of benzaldehyde (80%).

Effect of reusability of potassium perchlorate mediator
The aqueous phase of the potassium perchlorate obtained after the electrochemical oxidation was separated from the organic phase by phase separation, extracted twice (2 x 20 mL) with chloroform and the combined organic extract was worked up as usual to get benzaldehyde. The separated aqueous phase was recycled three times for the oxidation of benzaldehyde oxime and the results are reported in the Table 11. It shows that there is a regular

decrease in the yield of benzaldehyde, probably due to the handling loss of potassium perchlorate mediator on successive experiments. When 10% of potassium perchlorate were taken excess in each of the consecutive experiments to replenish the concentration of potassium perchlorate, benzaldehyde maintains constant at 80%.

Table 10. Influence of substrate concentration.

S.No.	Benzaldehyde oxime (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	5	72	24
2	**10**	**80**	**26**
3	15	79	26
4	20	76	25
Experimental conditions			
Organic phase: benzaldehyde oxime (5-20 mmol) in 25 mL chloroform	Aqueous phase	21.6 mmol KClO$_4$ + 10.2 mmol H$_2$SO$_4$ in 90 mL deionised water	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

Table 11. Influence of reusability of potassium perchlorate mediator.

S.No.	Amount of KClO$_4$ (mmol)	Benzaldehyde yield (%)	Current efficiency (%)
1	**21.6**	**80**	**26**
2	Reuse 1	79	26
3	Reuse 2	77	25
4	Reuse 3	73	24
Experimental conditions			
Aqueous phase: KClO$_4$ solution obtained from the first electrochemical reaction *(90 mL aqueous solution)	Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform	
	Current density	50 mA cm^{-2}	
	Passed charge	6 F/mol	
	Anode/Cathode	Pt/Pt	
	Temperature	30 - 40 ºC	
	Stirring rate	60 rpm	

* Additional 21.6 mmol KClO$_4$ were taken in each subsequent experiment.

Effect of reproducibility factor
The reaction was carried out under all the above mentioned optimal conditions four times. The results obtained are given in Table 12. It is observed that the yield remained almost similar for all the four times.

Table 12. Influence of reproducibility factor.

S.No.	Reproducibility factor time	Benzaldehyde yield (%)	Current efficiency (%)
1	**1**	**80**	**26**
2	2	79	26
3	3	80	26
4	4	81	26
Experimental conditions			
Organic phase	benzaldehyde oxime (10 mmol) in 25 mL chloroform		
Aqueous phase	21.6 mmol KClO$_4$ + 10.2 mmol H$_2$SO$_4$ in 90 mL deionised water		
Current density	50 mA cm^{-2}		
Passed charge	6 F/mol		
Anode/Cathode	Pt/Pt		
Temperature	30 - 40 ºC		
Stirring rate	60 rpm		

A possible mechanism for the electrocatalytic oxidation of benzaldehyde oxime to benzaldehyde in biphasic medium is outlined in the scheme below [17, 24].

$$KClO_4 \longrightarrow K^+ + ClO_4^-$$

$$ClO_4^- \xrightarrow{-e^-} ClO_4^{\cdot}$$
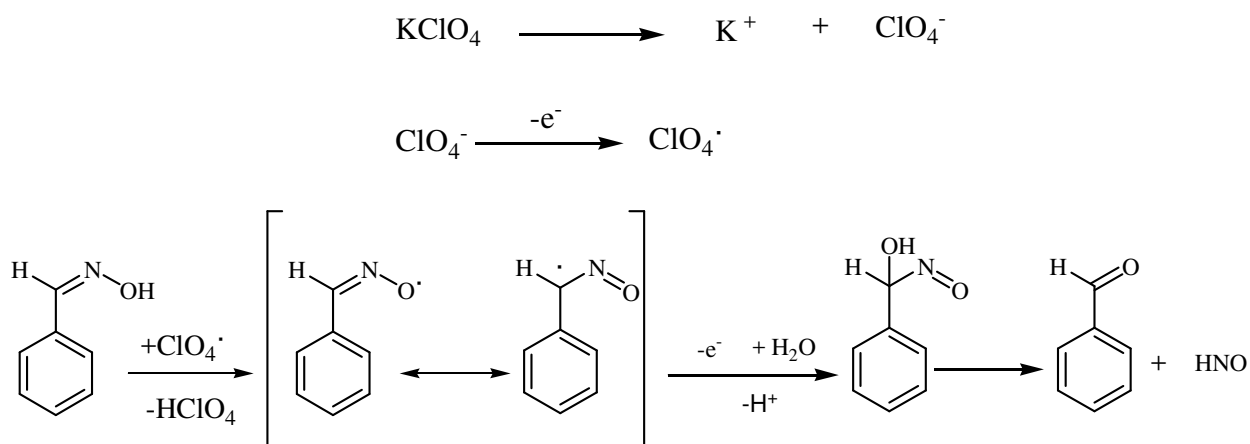
Scheme. Mechanism of electrochemical oxidation of benzaldehyde oxime.

The electrochemical oxidation of benzaldehyde oxime might have taken place through the following four steps.

  i. Perchlorate ion undergoes a one-electron oxidation and forms a perchlorate radical and it abstracts the hydrogen in the oxime.
 ii. Initial formation of an iminoxy radical by monoelectronic transfer and deprotonation.
iii. Transfer of a second electron and water addition leading to α-hydroxynitroso intermediate.
 iv. Decomposition of the latter resulting the benzaldehyde formation.

Conclusions
The electrochemical oxidation of benzaldehyde oxime to benzaldehyde by biphasic electrolysis constitutes a novel and efficient alternative method over conventional chemical methods.
With respect to the oxidation in homogeneous solutions, which, however, are still of considerable value, the heterogeneous of these reactions is currently an active field of research in industrial and academic chemistry. It is due to the simplified and easy handling procedures and work-ups. It is very important from a green chemistry point of view, easy and clean reactions and avoidance of by-products. Further advantages over conventional homogeneous reactions are typically higher selectivity, enhanced reaction rates and milder reaction conditions. Hence we find this as a novel method for obtaining carbonyl compounds from their corresponding oximes.

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