

*Full Paper*

## **Performance of Potassium Iodate as an Electrocatalyst for the Oxidation of Secondary Alcohols Utilizing a Platinum Electrode in a Biphasic Medium**

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**Abstract-** Potassium iodate was employed as a mediator with concentrated sulfuric acid to electrochemically oxidize substituted secondary alcohols in a biphasic medium with platinum electrodes. Using potassium iodate as a mediator in a biphasic medium, ketones were successfully generated from secondary alcohols. 1-phenyl ethanol is electrochemically oxidized to acetophenone in a biphasic medium. With maximum selectivity and good yields, the several substituted alcohols were successfully converted to ketones. The Platinum electrode had much more electrochemical activity and electrochemical products, according to the HPLC study that followed. The product aromatic ketones were described using UV, FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy, and the percentage of product yield was calculated using HPLC. Many secondary alcohols could also be converted to the appropriate ketones at room temperature, with isolated yields ranging from 80 to 95%. During recycling, the product's purity remained intact. It appears that this concept can grow while remaining pollution-free as a result.

**Keywords-** 1-Phenylethanol; Aromatic secondary alcohol; Biphasic medium; Platinum electrode; Potassium iodate

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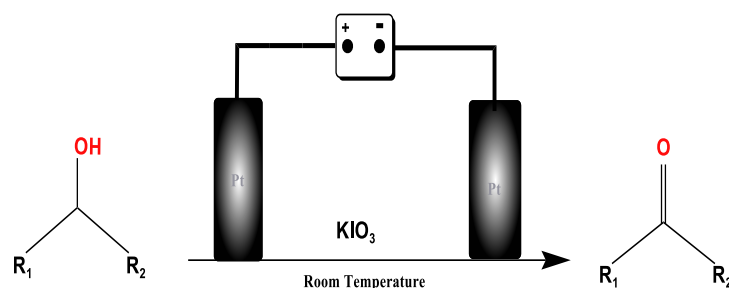
### **1. INTRODUCTION**

An increasing number of carbonyl compounds are required annually to produce fine chemicals, including food additives, medications, and fragrances [1,2,3]. One of the most

significant functional group changes in organic chemistry today is the selective oxidation of the corresponding primary and secondary alcohols to generate aldehydes and ketones [4,5,6,7]. Typically, conventional methods call for the use of reagents in stoichiometric or excessive concentrations, such as manganese, chromium, or hypervalent iodine [8,9,10]. Unfortunately, similar wastes would be produced by these oxidants, harming the ecosystem [11,12]. Interest in applying green chemistry, a well-known fundamental idea in chemical studies, to organic synthesis is growing [13]. A green catalyst needs to be utilized to synthesize the relevant carbonyl compounds in a sustainable and environmentally friendly manner.

The electrochemical synthesis method offers new possibilities for the synthesis of many high-quality chemicals because of its low cost, high atom utilization, and favorable effects on the environment [14–17]. Sodium nitrate acts as a useful redox mediator in a biphasic medium during the electrochemical process that produces aromatic aldehydes. Certain primary alcohols were replaced with strong electron-withdrawing groups, and secondary alcohols produced low product yields [18]. The oxidation of benzyl alcohols has been found to occur with a wide variety of oxidizing agents recently [19–22]. Recent advances in electro-organic synthesis, which substitutes environmentally benign reagents for conventional redox reactions, have opened up new possibilities for ecologically benign chemical processes.

In this study, we used platinum electrodes to oxidize alcohols to matching carbonyl compounds in potassium iodate utilizing a commercially available, non-toxic 1-phenyl ethanol as an electrocatalyst—a procedure that has never been reported before. because a higher yield than those based on the indirect anodic oxidation of secondary alcohols and their derivatives, catalyzed by redox systems, was obtained. The electrolysis system consists of an organic phase consisting of chloroform containing the substrate, an aqueous phase of 1.36 M sulfuric acid, and 80 mL of aqueous potassium iodate (2.3 mmol). Under these conditions, alcohols were oxidized at room temperature to the proper carbonyl compounds in a single-compartment cell, yielding good yields and needing the least amount of time to complete the electrolysis process. The advantages of the suggested method include low cost, easy scale-up, nearly no waste issues, and simple reaction conditions (low cell voltage, undivided cell, and constant current electrolysis with a cheap power supply). This work investigated the electrochemical behavior of potassium iodate for the oxidation of 1-phenyl ethanol to acetophenone on the Pt electrode to better understand the catalytic properties. There are currently very few papers on the synthesis of fine chemicals using the biphasic electrolysis approach. Our team recently developed a biphasic electrolysis device that converts benzyl alcohol to benzaldehyde electrochemically at ambient temperature. The electrochemical oxidation of substituted secondary alcohols to matching ketone compounds utilizing potassium iodate as a mediator with a Pt/Pt electrode combination is described here. The selective oxidation of secondary alcohols to ketones is emphasized in the current work (Scheme1).



The Electrocatalytic oxidations of Ketones from Secondary alcohols

**Scheme 1.** The electrocatalytic oxidations of ketones from secondary alcohol

## 2. EXPERIMENTAL SECTION

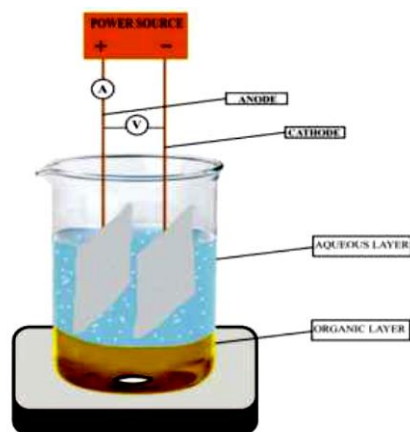
### 2.1 Preparation of Materials and Substrates

Sigma Aldrich and Fischer Scientific, India Pvt. Ltd. provided all the chemicals and solvents needed to perform electrolysis procedures without the need for additional purification. Analytical grade solvents from Alfa-Aesar and Sigma Aldrich Company include tetrahydrofuran, dichloromethane, acetonitrile, and chloroform. The source of all aqueous solutions is deionized water. The melting point was measured using an Elchem Lab melting point apparatus. HPLC was performed on a SHIMADZU LC-8A pump (250 mm X 4.6 mm used as stationary phase). The eluent was made using (80:20). The flow rate was maintained at 1 mL/min. Samples were analyzed at 254 nm using a UV detector.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected using a 500 MHz spectrometer, and FT-IR spectra using KBr pellets were collected using the Perkin-Elmer 100 Spectro chemical series.

### 2.2. The general protocol for selectively oxidizing secondary benzylic alcohol by electrochemistry

A solution of secondary benzylic alcohol (1.02 g, 10 mmol) and chloroform (20 ml) was put into a single-compartment electrolytic cell, and potassium iodate mediator (10 mmol) diluted in 80 ml of water was added to a 120 ml undivided beaker type-cell. To keep the medium acidic, the upper aqueous layer contains 1 g of potassium iodate as a mediator and 2 ml of sulphuric acid, while the bottom organic phase contains secondary benzylic alcohol for conductivity. The aqueous phase was then introduced with two platinum electrodes (each with a  $15\text{ cm}^2$  area) until they just touched the organic phase. The distance between the electrodes was fixed at 2 cm. The magnetic stirring was set to 40 rpm to keep the aqueous and organic phases biphasic. Galvano electrolysis was performed statically at room temperature and with a current density of  $50\text{ mA/cm}^2$ . After reaching 5F charges per mole of benzyl alcohol, the stirring was stopped. The lower organic phase, which contained the product, was separated using a separating funnel. The combined organic phase was washed twice with chloroform (2x25ml)

and dried over anhydrous sodium sulfate, with the solvent removed by residue distillation, confirming the presence of 95% ketones. Creating and tweaking the electrolysis settings resulted in high yields of desired products.



**Figure 1.** The oxidation of substituted secondary alcohols to corresponding ketones by biphasic electrolysis

### 2.3. Methodical Approach for 1-Phenylethanol Oxidation in Biphasic Medium

#### 2.3.1. The Effect at Room Temperature:

1-Phenylethanol (10 mmol) was combined with 20 ml of chloroform and a 120 ml undivided beaker-type cell received 80 ml of water with potassium iodate mediator (10 mmol) dissolved in it. For roughly an hour at room temperature, the solution was agitated at 50 rpm using a magnetic stirrer. While churning, the two layers the organic layer and the aqueous layer remain intact. 4  $\mu$ L were drawn and evaluated using HPLC for product analysis after an hour.

#### 2.3.2 Thermal Condition Reaction:

1-Phenylethanol (10 mmol) was combined with 20 ml of chloroform, and 80 ml of water was used to dissolve the potassium iodate mediator. A round-bottomed flask with a Liebig stirring rod was then added. For nearly an hour, the solution was left to boil. 4  $\mu$ L were drawn and evaluated using HPLC for product analysis after an hour.

#### 2.3.3. Electrochemical Method Reaction

The potassium iodate mediator (10 mmol) was dissolved in 80 ml of water and added to a 120 ml undivided beaker-type cell together with 1-phenyl ethanol (10 mmol), 20 ml of chloroform, and 80 ml of water. Platinum Anode and Platinum Cathode were carefully positioned inside the beaker cell so that the electrode layer would not come into contact with the organic phase that was situated at the bottom of the beaker cell. For one hour, the solution was stirred using a magnetic stirrer at 50 rpm. 4  $\mu$ L were taken after the electrolysis process was finished and evaluated with HPLC for product analysis.

## 2.4. Physical Characterization

Using TMS as an internal standard,  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  at 100 MHz or 125 MHz on a Bruker-500 NMR spectrometer to identify physical phases and compound synthesis. Using KBr pellets, IR spectra were captured on the Perkin-Elmer 100 Spectrochem series. On a SHIMADZU LC-8A pump (250 mm 4.6 mm) used as the stationary phase, HPLC was carried out. The eluent was made up of water and chloroform (80:20). A flow rate of 1 ml/min was maintained. Using a UV detector, samples were examined at a wavelength of 254 nm. All yields pertain to isolated products, and all chemicals were identified by comparing their spectral data and physical characteristics to those of the original sample. To make the potassium iodate solution and support electrolyte, deionized water was employed.

## 3. RESULTS AND DISCUSSION

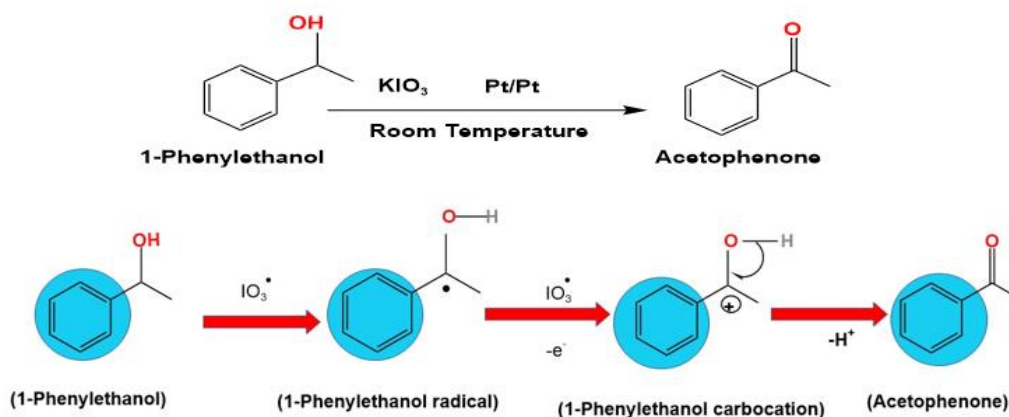
1-Phenyl ethanol was oxidized electrochemically in a potassium iodate at different conditions. It was carried out in an undivided cell at the optimum experimental conditions. Among these reaction conditions, an electrochemical reaction is one of the most effective reaction conditions shown in Table 1.

**Table 1.** Conditions for experimental oxidation process in biphasic medium

S. No	Reaction Condition	Temperature	Yields	Conditions
1	Room Temperature	Room Temperature	0%	Aqueous phase: Potassium iodate (1g) in water (80ml) Organic phase: Substituted Secondary alcohols(10mmol) in chloroform (20 ml)
2	Thermal	60-70 °C	20%	Aqueous phase: Potassium iodate (1g) in water (80ml) Organic phase: Substituted Secondary alcohols(10mmol) in chloroform (20 ml) Current passed: 5F/mole
3	Electro Chemical	30-35 °C	95%	Biphasic medium Aqueous phase: Potassium iodate (1g) in water (80ml) Organic phase: Substituted Secondary alcohols(10mmol) in chloroform (20 ml) Anode/Cathode: Pt / Pt (area = 15 cm <sup>2</sup> ) Current passed: 5F/mole

### 3.1. Proposed Electrochemical Oxidation Mechanism

For the current inquiry, a potential response mechanism is put forth (Scheme 2). One electron transfer that takes place while the reaction develops in the aqueous phase results in the creation of the intermediate iodate radical. The unstable iodate is radical produced in situ and combines with the substrate in the organic phase to produce benzylic radical species after quickly oxidizing the alcohols in the interfacial region. Following cleavage, these benzylic radical species produce the desired product.



**Scheme 2.** Electrochemical oxidation of 1-phenyl ethanol to acetophenone

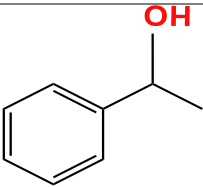
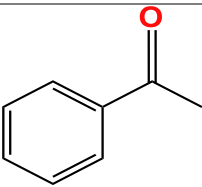
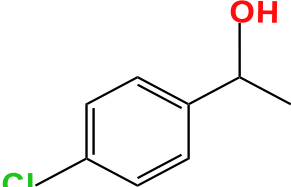
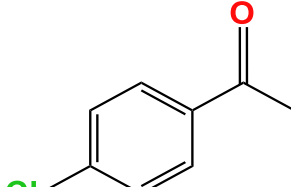
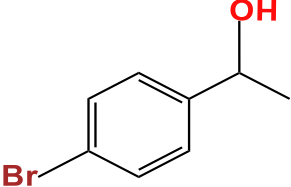
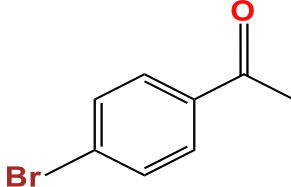
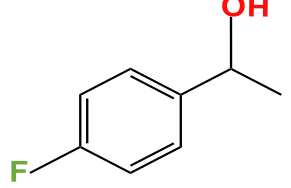
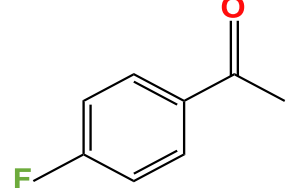
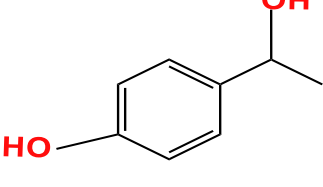
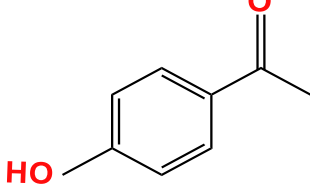
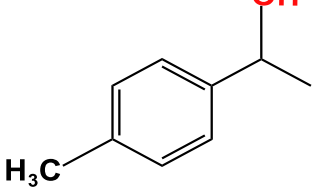
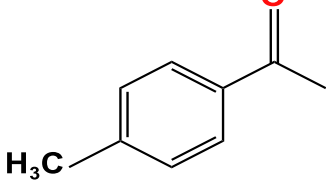
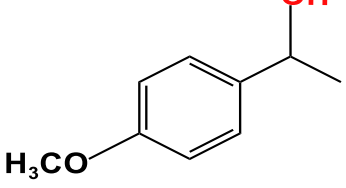
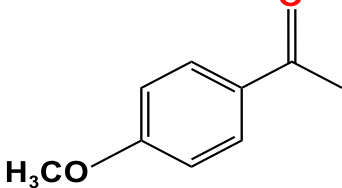
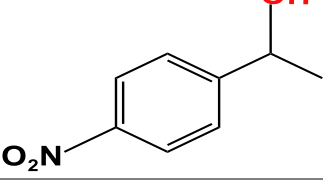
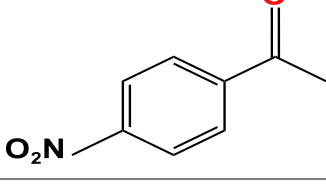
### 3.2. Aromatic secondary alcohols are oxidized electrochemically in a biphasic medium

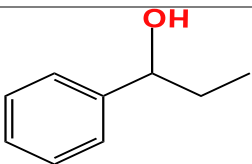
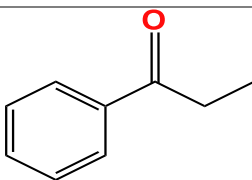
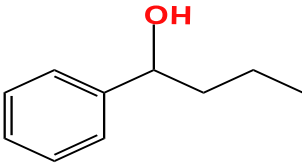
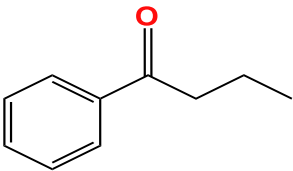
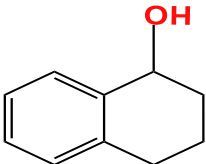
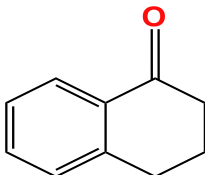
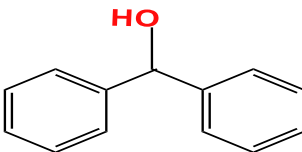
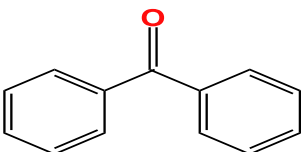
To assess the universality of the reaction, various aromatic secondary alcohols were investigated at their best. The results are presented in Table 2. A good product (95%), produced by the electrochemical oxidation of 1 phenyl ethanol in a biphasic system with a charge density of 5 F/mol. This biphasic approach produced matched carbonyl compounds from substituted secondary alcohols in high yields in a single-compartment reaction. The yields of the various commodities are displayed in Table 2.

This method of biphasic electrolysis prevented further oxidation to acid. The results are summarised in Table 2. The product ketones were recognized using HPLC. The peak regions of the corresponding experimental products were identified using actual samples to calculate yield. The alcohols and other compounds were purchased from Sigma-Aldrich, Alfa-Aesar, and Merck. Before use, they received no further purification. Potassium iodate was employed as a less expensive redox mediator to successfully carry out the selective oxidation of aromatic alcohols in biphasic electrolysis. In-situ generation of the iodate radical, a potent hydrogen abstractor, is made possible by the iodate ion's one-electron oxidation in the aqueous phase.

Inspired by these results, the scope of this electrochemical method for the oxidation of secondary alcohols was explored. As shown in Table 1, 1-phenylethanol could be converted completely to acetophenone in 95% yield (entry 1).

**Table 2.** Electrochemical oxidation of substituted secondary alcohols

Entry	Substituted Secondary Alcohol	Charge Passed (F/mol)	Time	Product	Yield (%)
1		5	145		95
2		5	140		92
3		5	140		91
4		5	140		90
5		5	140		85
6		5	140		89
7		5	130		87
8		5	95		88

9		5	120		76
10		5	120		74
11		5	80		75
12		5	85		68

**Biphase electrolysis conditions**Current density: 50 mA/cm<sup>2</sup>

Electrodes : Platinum: Platinum

Temperature : Room temperature

Stirring rate : 50 rpm

Aqueous phase: Potassium iodate (5mmol) in water (80 ml)

Organic phase : Substituted Secondary alcohols(10mmol) in chloroform (20 ml)

Similarly, a series of secondary benzyl alcohols with both electro-donating and electron-withdrawing substituents in the phenyl group were provided in good to excellent isolated yields (entries 2-8). For example, four secondary benzylic alcohols with an electro-donating group were converted into the corresponding ketones with good isolated yields under standard conditions (entries 5-8). Meanwhile, halide substituent products such as 4-chloro acetophenone, 4-bromo-acetophenone, 4-fluoro-acetophenone and 4-hydroxy-acetophenone were all obtained 92%,91%,90% and 85% in excellent isolated yields (entries 2-4). We discovered that the smooth oxidation of aromatic alcohols replaced with electron-donating groups, such as -methyl and -methoxy groups, yielded 89% and 87%, respectively, with 5 F/mol current (entries 6-7). The substituted aromatic alcohol with a strong electron-withdrawing group (entry 8) yielded 88% ketones due to the -nitro group's high solubility in chloroform solvent.

It was possible to complete the conversion with an isolated yield of 76% when the substrate 1-phenylpropan-1-ol was utilized (entry 9). Furthermore, the substances 1-phenyl-1-butanol, 1-Tetralol and benzhydrol have excellent results (entries 10-12).

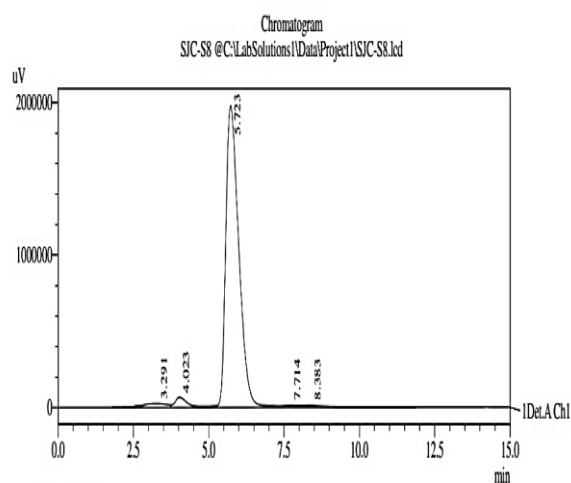


### 3.3. Characterization of the Product

The product obtained after electrolysis was characterized by different spectroscopic analyses such as UV, FTIR,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR. From HPLC data, the percentage of product yield was calculated.

Spectral details of acetophenone are as follow:

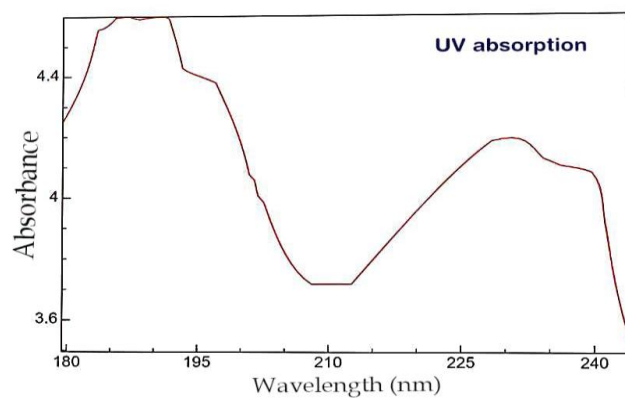
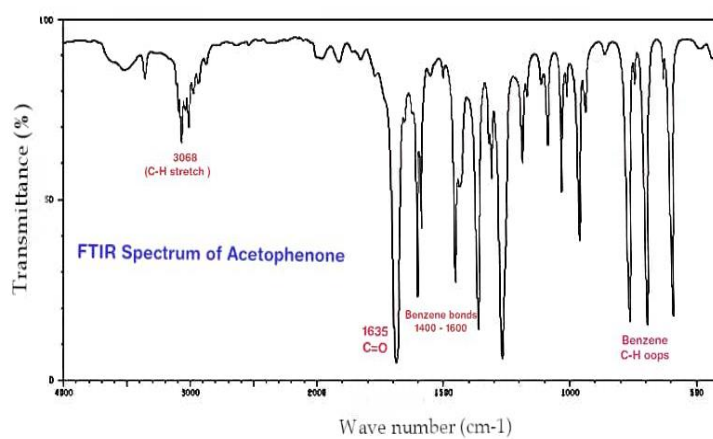
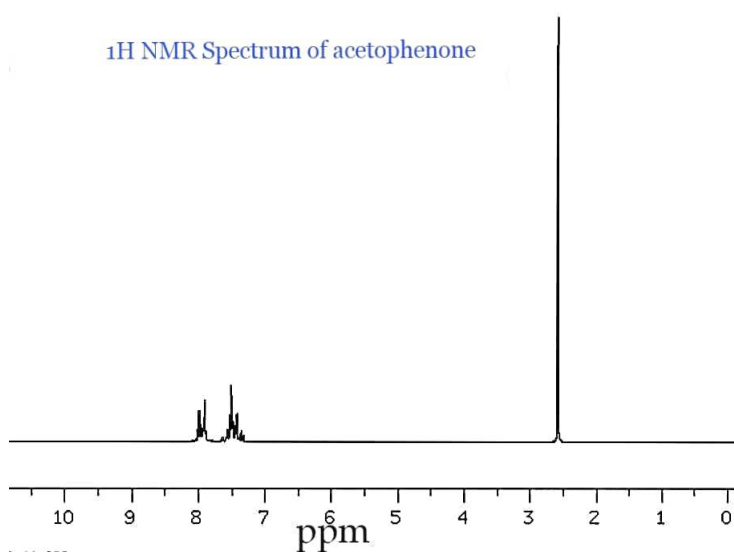
- Colorless oil, yields 95%
- HPLC retention time of acetophenone: 2.25 min
- UV SPECTRUM: UV spectrum of benzaldehyde in water shows the maximum wavelength  $\lambda_{\text{max}}$  at 244 nm.
- FTIR SPECTRUM:  $\text{cm}^{-1}$  v: 850 (aromatic C-H bending) 1600-1451 (Benzene bonds stretching frequency) 1635 (C=O Stretching) 3068 (aromatic C- H stretching)
- $^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.94–7.92 (m, 2H), 7.55–7.51 (m, 1H), 7.44–7.41 (m, 2H), 2.57 (s, 3H).
- $^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.0, 136.9, 132.9, 128.4, 128.1, 126.4.

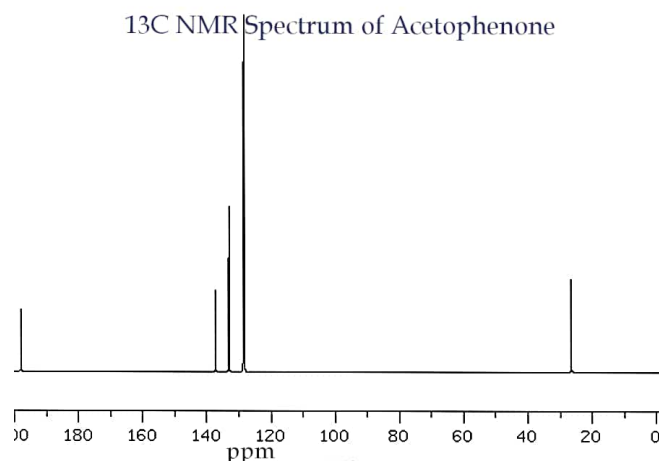


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.291	1611496	28668	2.501	1.369
2	4.023	1928744	66853	2.994	3.193
3	5.723	60284671	1980633	93.568	94.604
4	7.714	207606	7312	0.322	0.349
5	8.383	396301	10127	0.615	0.484
Total		64428818	2093593	100.000	100.000

**Figure 2.** HPLC data for acetophenone

**Figure 3.** UV spectrum of acetophenone**Figure 4.** FTIR spectrum of Acetophenone**Figure 5.** <sup>1</sup>H-NMR spectrum of Acetophenone



**Figure 6.**  $^{13}\text{C}$ -NMR spectrum of Acetophenone

#### 4. CONCLUSION

Finally, it has been investigated how the iodate radical behaves electrochemically when 1-phenyl ethanol is oxidized in a biphasic medium. Electrochemical tests showed that potassium iodate had a lower potential and displayed reversible redox activity. Single-electron oxidation produced the iodate free radical. 1-phenyl ethanol is used to create acetophenone. A range of substrates, such as aromatic, heteroaromatic, and aliphatic secondary alcohols, could be converted to the corresponding ketones with good to exceptional yields when reaction conditions were mild. Platinum electrodes have been effectively employed to convert alcohols into ketones in a selective manner. In conclusion, platinum, platinum electrodes, and potassium iodate mediators are less expensive chemicals that were used in biphasic electrolysis at low temperatures to selectively oxidize aromatic alcohols at the outside temperature. Regarding simplicity of handling, atom utility, and the ability to recycle used mediators, this technique offers more benefits than homogenous systems. In every oxidation reaction, selectivity better than 95% was observed. Unlike typical oxidation processes, the biphasic electrolysis setup is so straightforward that reactions can occur there. Overall, the suggested electrochemical procedure and reaction setup is straightforward and help to some extent make synthesis more environmentally friendly. It possessed many benefits, including no secondary products, low production costs, selective oxidation, high current efficiency, and high yield and reuse of old mediators. During recycling, the product's purity remained constant. Therefore, it appears that this plan can be scaled up as a pollution-free process.

#### Declarations of interest

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

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