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Electrochemical conversion of benzene sulphonyl azide into sulphonamide assisted by sodium ascorbate

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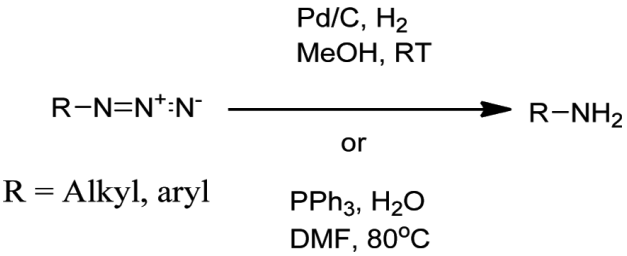
Chemical reduction of organic azides is a commonly accepted route in synthetic organic chemistry to prepare amino compounds. Researchers and scientists are interested in choosing greener pathways in the course of the synthesis of organic molecules. In the present work we report the synthesis of benzene sulphonamide by the electrochemical reduction of benzene sulphonyl azide using platinum electrodes. Influence of current density and voltage, effect of electrolytes, effect of solvents and effect of substrate concentration on the yield of the product have been studied. The reaction is more feasible in the presence of sodium ascorbate (in 1:1 methanol-water) which acts as both supporting electrolyte and electron transferring agent in the electrochemical process.

Keywords: Sulphonyl azide, Electrochemical reduction, Sodium ascorbate, Cyclic voltammetry

Use of electrochemical methods are considered as a greener strategy in organic synthesis, in which organic molecules are converted into useful intermediates or fine chemicals[1,2]. The electro-chemical approach is effective for performing key classes of processes, including oxidations and reduction[3]. During electrochemical reactions, one of two things can occur: either an electron will be transferred to the substrate, resulting in a reduced product, or the compound loses an electron, which will result in an oxidised product[4]. Utilizing an electrolyte is the most effective way to pass current through to the substrate[5].

In general, electrochemical organic transformations are considered green since these processes are not accompanied by unwanted byproducts[6,7]. Less feasible chemical reactions may run smoothly if it is performed *via* electrochemically[8]. In the last few decades, electrochemical transformations such as reduction, oxidation, cyclization, cycloaddition *etc*. have been explored by many researchers[9-11]. Unpredictability of the products, release of toxic gases, difficulty in explaining the mechanistic pathway *etc*. are considered as some drawbacks of electrochemical synthesis[12]. Even though some inherent limitations are associated with the electrochemical synthesis, they are unquestionably more eco-friendly than the conventional chemical processes[13].

In organic synthesis, azide is used as an important precursor for amino compounds[14,15]. Azides can be reduced easily *via* Staudinger reduction (Scheme 1)[16,17]. In this work, we have prepared benzene sulphonyl azide from benzene sulphonyl chloride and sodium azide by chemical methods. We succeeded in converting the prepared azide to benzene sulphonamide electrochemically. Sodium ascorbate was used as the supporting electrolytic medium and Pt electrodes were used to perform the electrochemical synthesis. The process was studied under varying conditions of current density, voltage, electrolytes, solvents and substrate concentrations to find out the optimum condition.



Scheme 1 — Staudinger reduction

Experimental Section

All chemicals were purchased from Merck Millipore and supplied by Chemind Thrissur. NMR and FTIR spectra were recorded on Bruker AV 400 MHz spectrometer ($CDCl_3$ solvent) and Perkin–Elmer FT-IR spectrometer (ATR method) respectively. Cyclic voltametric studies were done using CH1660D instrument in a three-electrode cell (Ag/AgCl: reference electrode, Pt: counter electrode, Glassy carbon: working electrode).

Synthesis of sulphonyl azide

A 10 mmol solution of benzene sulphonyl chloride was dissolved in 30 ml acetone at 0 ^{o}C and a 20 mmol solution of sodium azide in 25 ml water was added drop wise. After a period of 3 h stirring, the reaction mixture was diluted with water and the product formed was extracted with ethyl acetate and the solvent was evaporated under reduced pressure condition. The obtained sample was pure enough to perform the electrochemical synthesis.

Electrochemical reduction of azide

A 3 mmol solution of benzene sulphonyl azide was dissolved in 1:1 methanol-water mixture (50 ml). To this mixture, 3 mmol sodium ascorbate was added and inserted two platinum electrodes (4×4 cm). A potential of 30 V was applied between the electrodes for 3 h. A gradual rise in the temperature was noticed during the progress of the reaction. Completion of the reaction was assured with the help of TLC. The reaction mixture was cooled, diluted with 50 ml of water and extracted the product with ethyl acetate. The organic layer was dried over sodium sulphate and the evaporation of the solvent was done under reduced pressure conditions.

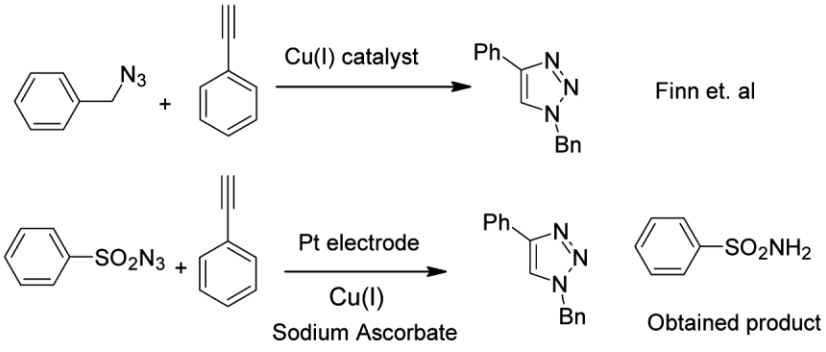
In order to investigate the optimum conditions, operational parameters such as applied potential, current density, electrolytes, solvents and substate concentration were varied and the electrochemical synthesis was performed.

Results and Discussion

Finn *et al*[17] have reported the cycloaddition reaction between the azide and alkyne under electrochemical conditions using Cu(I) catalyst to produce 1,2,3-triazole (Scheme 2). We tried a similar reaction with benzene sulphonyl azide, phenylacetylene and Cu(I) chloride in methanol-water mixture using Pt electrodes. It was noted that no reaction was taking place under these conditions and noted that addition of sodium ascorbate initiated the process. Unexpectedly we noticed that the reaction follows a different pathway as shown in Scheme 2. Instead of cycloaddition reaction, the benzene sulphonyl azide underwent electrochemical reduction to benzene sulphonamide. Repeated experiments revealed that the reaction was initiated only in the presence of sodium ascorbate and also established that Cu(I) has no role in the electrochemical synthesis. The product was retrieved by treating the mixture with 2 M HCl to get the salt and then neutralized the mixture. The sulphonamide precipitated was extracted with ethyl acetate and evaporated the solvent under reduced conditions. Benzene sulphonamide was characterized by its melting point (151^{0}C) and spectral analysis (FTIR; $\nu_{N\text{-}H}$ 3359 cm^{-1}, $\nu_{S=O(sym)}$ 1180 & 1152 cm^{-1}, $\nu_{S=O(asym)}$ 1352 &1310 cm^{-1}. ^{1}HNMR: δ_{NH2} 7.59(s), $\delta_{ArC\text{-}H}$ 7.36-7.84 ppm. ^{13}CNMR: 126, 129.4, 132.3, 144.6 ppm). To optimize the reaction conditions, we performed the electrochemical process by varying the different parameters such as current density, applied voltage, solvents, electrolytes and concentration of sulphonyl azide.

(a) Effect of Voltage

Influence of the applied potential on the yield of sulphonamide was studied for the electrochemical



Scheme 2 — Comparison of chemical and electrochemical syntheses

reduction of sulphonyl azide (3 mmol) using 1:1 methanol-water mixture (50 ml) and sodium ascorbate (3 mmol) as electrolyte. The voltage varied from 5 to 30 and the reaction period was maintained at 3 h. It was noted that the yield of benzene sulphonamide proportionally increased with the applied voltage and reached a maximum at 20 V (93.7%). Though further increase of the potential did not exhibit an appreciable rise in the yield of the product, 30 V was chosen as the optimum voltage for the electrochemical synthesis, since the reaction displayed appreciable rate at this potential when compared to the lower potentials. It was observed that reaction was completed in approximately 2.5 h at this higher potential. Table 1 and Fig. 1 represent the variation of applied potential on the yield of product.

(b) Effect of current density

The current density (current/area) of the electrochemical synthesis varied from 5 to 50 mA/cm^2. All the experiments were performed at a constant potential of 30 V. 3 mmol sodium ascorbate and 1:1 methanol-water mixture was used for the process. The yield of benzene sulphonamide was found to increase with current density and reached to 93.8% at I=40 mA/cm^2. After this, no appreciable change in the yield of the product was observed with increase current density. The experimental data is shown in Table 2 and the variation of current density on the yield of the product is depicted in Fig. 2.

(c) Influence of Solvents

To study the effect of solvents on the yield of sulphonamide, various solvent-water mixtures (1:1) along with sodium ascorbate electrolyte were tried in the electrochemical synthesis. Organic solvents such as methanol, ethanol, acetonitrile, and chloroform were used to perform electrochemical reduction at a constant voltage of 30 using Pt electrodes. 50 ml of solvent-water mixtures were taken in each experiment and benzene sulphonyl azide and sodium ascorbate (3 mmol each) were added and performed the electrochemical synthesis. Time of the reaction was maintained at 3 h. Among various solvents used, methanol-water mixture gave a maximum yield of 93.8%. The enhanced yield of benzene sulphonamide during electrochemical synthesis may be attributed to the high polarity and less steric effect of the methanol. In addition to this, the potency of the ascorbate as an electron transferring agent is completely demonstrated

Table 1 — Influence of potential on the yield of benzene sulphonamide

Sl. No.	Potential (V)	Yield of benzene sulphonamide (%)
1	30	93.8
2	25	93.6
3	20	93.7
4	15	72.2
5	10	52.8
6	5	29.6

Table 2 — Variation of current density on the yield of benzene sulphonamide

Sl. No.	Current Density (mA/cm^2)	yield of benzene sulphonamide (%)
1	5	32.5
2	10	55.4
3	20	88.2
4	30	91.1
5	35	93.2
6	40	93.8
7	50	93.7

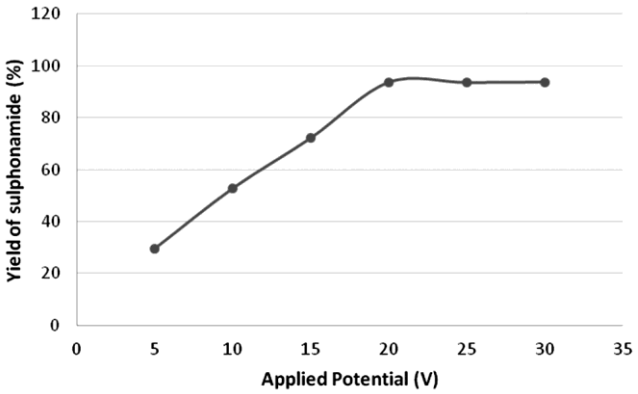


Fig. 1 — Variation of applied potential with the yield of sulphonamide

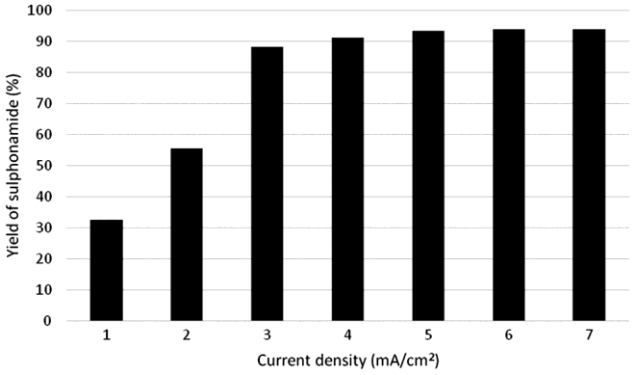


Fig. 2 — Plot of current density against the yield of benzene sulphonamide

in the methanol-water mixture. The influence of solvent is tabulated in the Table 3.

(d) Influence of Electrolytes

Table 4 shows the effect of various electrolytes (3 mmol) on the yield of benzene sulphonamide. Solvents such as tert-butyl ammonium bromide, sodium chloride, potassium chloride and sodium ascorbate were employed in the electrochemical reduction of benzene sulphonyl azide (3 mmol) at 30 V in 1:1 methanol-water (50 ml) medium using Pt electrodes. From the table it is evident that the yield of the benzene sulphonamide was very high in the presence of sodium ascorbate compared to other electrolytes. The ability of the ascorbate ion to intervene in the electrochemical process as an electron transferring agent (Fig. 3) is the main reason for the increased yield of the benzene sulphonamide. Additionally, sodium ascorbate acted as a supporting electrolyte to provide a good medium of conductance in 1:1 methanol-water system. In the absence of the electrolyte, the reaction was not progressed due to the poor conducting nature of the medium.

(e) Effect of substrate concentration

Electrochemical reduction of benzene sulphonyl azide to sulphonamide was carried out at various substrate concentrations (1mmol – 3 mmol) at optimum experimental conditions such as 1:1 methanol-water mixture (50 ml), 3 mmol sodium ascorbate, 30 V applied potential and at a current density of 40 mA/cm^2 for a period of 3 h using Pt electrodes. The experimental data is provided in Table 5. It is observed that, 3 mmol concentration of sulphonyl azide gave a maximum yield of sulphonamide (93.8%). No appreciable correlation was observed between the amount of benzene sulphonyl azide and the yield of benzene sulphonamide.

Cyclic voltametric studies

To get an insight into the mechanism of electrochemical process, cyclic voltametric studies were performed. Fig. 4 displays the combined CV plots of sodium ascorbate, benzene sulphonyl azide and the reaction mixture. All experiments were conducted in 1:1 methanol-water mixture. Neither sodium ascorbate nor sulphonyl azide gave well defined redox peaks during the scanning process. But the reaction mixture showed an oxidation peak at 1.26 V at a scan rate of 50 mV/s. This may be attributed to the electrochemical response shown by the product molecule benzene sulphonamide. The oxidation taking place in the sulphonamide at the surface of glassy carbon electrode can be explained as follows:

Table 3 — Influence of solvents on the yield of benzene sulphonamide

Sl. No.	Solvent (1:1)	Yield of benzene sulphonamide (%)
1	Methanol:H_2O	93.8
2	Ethanol:H_2O	91.2
3	CH_3CN:H_2O	44.4
4	$CHCl_3$:H_2O	12.3

Table 4 — Effect of solvents on the electrochemical reduction of benzene sulphonyl azide

Sl. No.	Electrolyte	Yield of benzene sulphonamide (%)
1	No electrolyte	No reaction
2	$tBuN^+Br^-$	46.6
3	NaCl	31.3
4	KCl	58.0
5	Sodium ascorbate	93.8

Table 5 — Influence of substrate concentration on the yield of sulphonamide

Sl. No.	Benzene sulphonyl azide (mmol)	Yield of benzene sulphonamide (%)
1	3	93.8
2	2.5	93.6
3	2	93.6
4	1	93.5

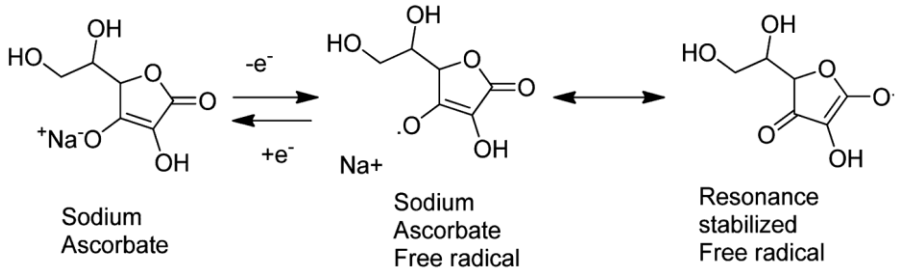


Fig. 3 — Stabilisation of ascorbate radical

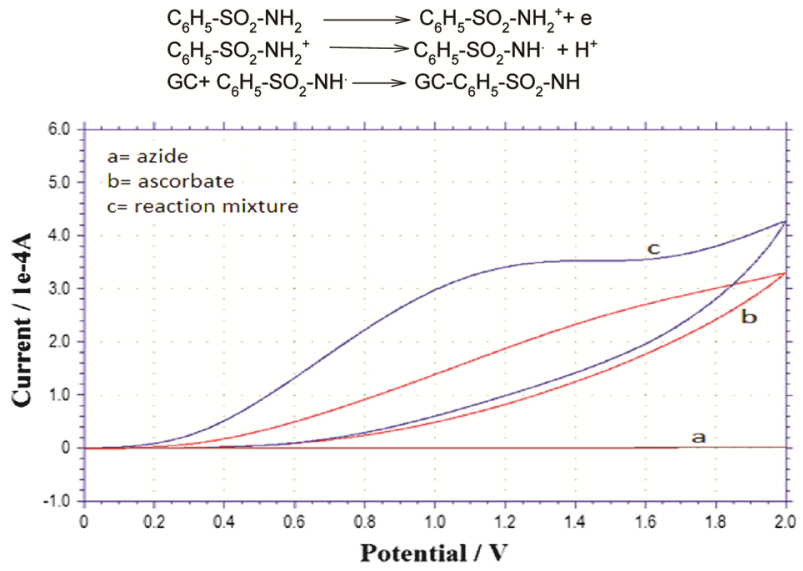


Fig. 4 — Combined cyclic voltammograms of azide, ascorbate and reaction mixture

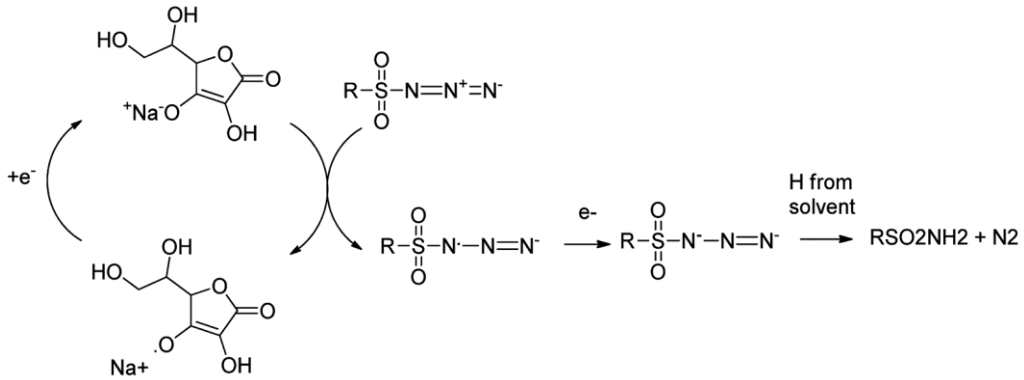


Fig. 5 — Plausible reaction mechanism

It can be concluded that the electrochemical reduction of sulphonyl azide was not visible in the cyclic voltametric experiments.

Mechanism

The plausible mechanism of the electrochemical reduction of benzene sulphonyl azide can be explained as follows. Sodium ascorbate donates one electron to benzene sulphonyl azide and converts into an ascorbate radical. The unstable ascorbate radical is stabilized by resonance and abstracts one electron from the current source and move back to the original state. Meanwhile, reduction takes place for the sulphonyl azide which accepts two protons from the solvent molecules to produce benzene sulphonamide. The role of sodium ascorbate as an electron transferring agent was proved in this study and it is noted that no electrochemical process starts in the absence of sodium ascorbate. The mechanism of the entire process is summarized in the Fig. 5.

Conclusion

In this article we report a green, facile and cost-effective method for the synthesis of benzene sulphonamide starting from benzene sulphonyl azide and sodium ascorbate. The reaction conditions were optimized for the applied potential, current density, solvent, electrolyte and substrate concentrations. A very good yield (93.8%) of the benzene sulphonamide was obtained during the electrochemical process at 30 V and current density of 40 mA/cm^2 in 1:1 methanol-water mixture (50ml) using Pt electrodes. Cyclic voltametric studies of the reactants and reaction mixture were carried out to elucidate the electrochemical response of the system. The dual behaviour of sodium ascorbate both as an electron

transferring agent and supporting electrolyte was well established in this study. Possible mechanism of the electrochemical reduction is also explained in this work.

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