



A Facile and Convenient Method to Reduce Organo azides Under Electrochemical Condition and Investigation of the Process thorough Cyclic Voltammetry

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ABSTRACT

Organo azides are potential precursors for the preparation of amines by different ways of chemical reduction. In the present studies, a simple and more convenient method was developed to reduce to the corresponding amine or sulphonamide under electrochemical condition using sodium ascorbate as the promoter and platinum electrodes. The reduction was achieved with sulfonyl azides, alkyl and aryl azides with moderate to quantitative yields. Cyclic voltammetry studies were carried out to study this electrochemical reduction.

Keywords: Azide reduction, Electrochemical reaction, Sulphonamides, Sodium ascorbate.

INTRODUCTION

Electrochemical transformation of organic compounds into useful intermediates or fine chemicals is an interesting approach in organic synthesis as they are greener reactions compared to reactions that involve reagents.¹ Oxidations and reductions are important classes of reactions achieved by electrochemical method.² In electrochemical reactions either electron is delivered to the substrate to give reduced product or the compound lose the electron to give oxidized product.

The passage of current through the substrate is better achieved by using electrolyte, a medium in which electrons are present in a mobile state.

Even though the electrochemical reactions are used for oxidations and reduction reactions of metal salts since the first report by Alessandro Volta in 1800,³ organic reactions were less explored for many years. In the last few decades, several organic transformations including oxidations, reductions,⁴ palladium-catalyzed cross coupling reactions,⁵ C-H functionalization cycloaddition,⁶ intramolecular



cyclization⁷ etc. have been studied extensively under electrochemical condition. The advantages of organic electrochemical reactions include the simple set up and environmentally friendliness. These reactions can be considered as green reaction as the reagent is only electron and no harmful by-product is produced in the reaction. Also, some of the organic electrochemical reactions which proceed smoothly under electrochemical condition are less favored or less probable under traditional non-electrochemical method⁸. Even though electrochemical reaction suffers drawbacks such as the liberation of toxic gases during the reaction, formation of undesired side-products, unpredictability of the product in the reaction, understanding the exact mechanistic pathway etc., undoubtedly, they are green and more powerful route to organic synthesis.⁹

Azide is one of the precursors for amine functional group and it is relatively easy to introduce azide by substituting the leaving groups like sulphonate ester or halide with readily accessible sodium azide (NaN_3).¹⁰ Since azide group is non-polar and does not react with most of the functional groups, azide functionality often serves as non-reactive precursor for amine. In organic synthesis, azide is generally reduced by using Pd/C, H_2 or PPh_3 , H_2O , popularly known as Staudinger reduction.¹¹ Reduction with Pd/C, H_2 is less selective and hence Staudinger reduction is often preferred as the condition is more selective and reduces only azide Figure 1.

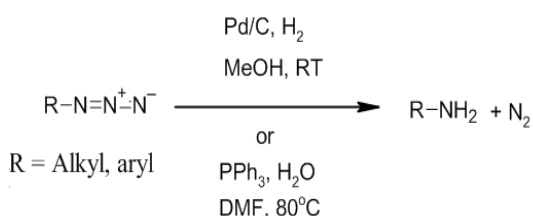


Fig. 1. Azide reduction

Considering the abundance of nitrogen containing compounds in nature and drug molecules,¹² it is worthy to develop a simple and robust method to introduce nitrogen functional group. In this communication, we report a simple method to reduce organo azide to the corresponding amine or sulphonamide electrochemically using sodium ascorbate and Pt electrodes.

EXPERIMENTAL

All melting points were measured on a Büchi

535 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 MHz digital NMR spectrometer in CDCl_3 or DMSO-d_6 . The solvents were purified and dried by standard procedures prior to use; petroleum ether of boiling range 60–80°C was used for column chromatography. Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer. All evaporations were performed under reduced pressure. For column chromatography, silica gel (60–120 mesh) was employed.

General procedure for the preparation of sulphonyl azide

To a solution of sulphonyl chloride (10 mmol) in acetone (30 mL) at 0°C, a solution of sodium azide (20 mmol) in H_2O (30 mL) was added drop wise. The reaction mixture was stirred for 3 h at the same temperature and slowly brought to room temperature. Later on, the reaction mixture was diluted with water and extracted thrice with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The crude was pure enough and taken as such for electrochemical reduction.

General procedure for the preparation of aryl azide

Aromatic amine (10 mmol) and dil. HCl (10 mL, 2N) was taken in a conical flask. The reaction mixture was cooled to below -15°C using ice and salt freezing mixture. To this a solution of NaNO_2 (20 mmol) in water (5 mL) was added dropwise. The resulting yellowish brown froth is stirred well for 5 to 10 min at the same temperature. After the evolution of N_2 is ceased, sodium azide (20 mmol) in 5 mL water is added dropwise and stirred for 30 minutes. The solution was slowly brought to room temperature. The reaction mixture was diluted with water and extracted thrice with ethyl acetate. The combined organic layer was concentrated under reduced pressure. The crude was purified using column chromatography using Pet. ether:ethyl acetate (95:5) to get the aryl azide as yellowish viscous liquid.

General Procedure for the preparation of benzyl azide

To a solution of the benzyl halide (10 mmol) in DMF was added NaN_3 (12 mmol) and heated at 60°C until the reaction is completed. The reaction mixture was diluted with water and extracted thrice

with ethyl acetate. The combined organic layer was concentrated under reduced pressure and purified with the aid of column chromatography using Pet. ether:ethyl acetate (95:5) to get the benzyl azide as yellowish viscous liquid.

General procedure for the electrochemical reduction of azide

To a solution of the azide (3 mmol) in methanol: water mixture (50 mL, 1:1) in 100 mL beaker sodium ascorbate (3 mmol) was added and the platinum electrodes were immersed in the reaction mixture. An electric current of 30V was applied to the reaction mixture for three hours. During the time there was gradual increase in the temperature. After completion of the reaction, as indicated by the TLC, the reaction mixture was diluted with more water (50 mL) and extracted thrice with ethyl acetate. In the case of aryl/alkyl azide, the reaction mixture was subjected to acid work to get the amines as their salt in water which was further neutralized and extracted with ethyl acetate. The combined organic layer was dried over sodium sulphate and concentrated under reduced pressure to get the crude compound which was subjected to column chromatography using silica gel and pet ether: ethyl acetate (70:30) as eluent.

In this experimental work, electrochemical reduction of sulfonyl azides to the corresponding amides was studied by using platinum electrodes. Various sulfonyl azides were investigated under different conditions and reductions were monitored. From a green chemistry point of view, this method will be useful because of the ease of work, selectivity, energy efficient and environmentally safe world. Further, the replacement of the conventional chemical reactions by use of electrochemical processes increases the efficiency and reduces the generation of waste from expensive reagents.

Cyclic voltammetry

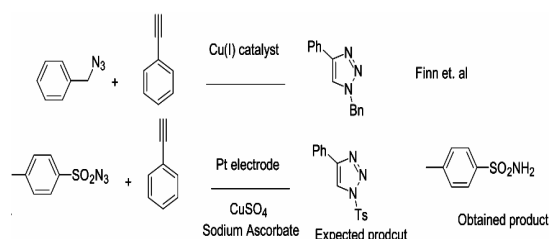
To understand the electrochemical behaviour of the reaction cyclic voltametric studies were performed. Ag/AgCl electrode, Glassy carbon electrode and Platinum electrode were acted as reference, working and counter electrodes respectively in the electrolytic cell. Each analysis was done after cleaning the working electrode with the emery paper to remove the adhered impurities. Voltammograms of sodium ascorbate, organic azide

and the reaction mixture were independently recorded in the range 0-2 V and at a scan rate of 50 mV/s. CV studies of the reaction mixture were also performed at various scan rates (10-50 mV/s) to establish the electrode kinetics. Sodium ascorbate itself acted as supporting electrolyte during CV analyses to make the solution a good conductor of current.

RESULTS AND DISCUSSION

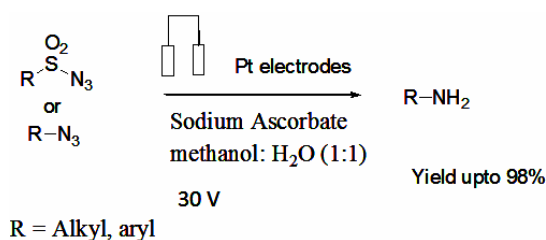
Synthesis and characterization

Dipolar cycloaddition between azide and alkyne is one of the most studied methodology to obtain 1,2,3-triazole and has emerged as very popular click reaction. Finn *et al.*,¹³ successfully achieved this cycloaddition between azide and alkyne to give 1,2,3-triazole under electrochemical condition using electrochemically protected copper(I) catalyst. In our lab, we attempted the cycloaddition between sulphonyl azide and alkyne under electrochemical condition to get 1-sulfonyl phenyl 1, 2, 3-triazole derivatives that are precursors for α -diazo imines.¹⁴ Tosyl azide (TsN_3), phenyl acetylene, sodium ascorbate in methanol were subjected to electrochemical reaction using Pt electrodes with CuSO_4 in catalytic amount (1 mL) at room temperature. Unexpectedly, we observed the azide reduction product i.e sulphonamide instead of the expected [3+2] cycloaddition product (Scheme 1). In the literature it is shown that the acyl azide can be reduced under electrochemical condition.¹⁵



Scheme 1

Surprised by this observation, we thought of investigating the reduction of azides under electrochemical condition. Accordingly, sulphonyl azide was subjected to electrochemical reaction with sodium ascorbate in methanol:water (1:1) as solvent. Water improves the solubility of sodium ascorbate. Platinum plates (4x4 cm) were used as electrodes and a constant voltage of 30V was applied for a period of 3 hours. It is noteworthy that the reduction took place even in the absence of copper sulphate (Scheme 2).



Scheme 2. Electrochemical Reduction of azide

Table 1: Standardization of reaction conditions^a

Sr. No	Electrolyte	Solvent	Potential(V)	% Yield ^b
1	No electrolyte	Methanol:H ₂ O	30	No reaction
2	tBuN+Br-	Methanol:H ₂ O	30	48
3	NaCl	Methanol:H ₂ O	30	33
4	Sodium ascorbate	Methanol:H ₂ O	30	98
5	Sodium ascorbate	Ethanol:H ₂ O	30	96
6	Sodium ascorbate	CH ₃ CN:H ₂ O	30	45
7	Sodium ascorbate	CHCl ₃ :H ₂ O	30	15
8	Sodium ascorbate	Methanol:H ₂ O	20	98
9	Sodium ascorbate	Methanol:H ₂ O	10	55c
10	Sodium ascorbate	Methanol:H ₂ O	5	32d

^aReaction condition: Pt electrodes, tosyl azide (3 mmol), electrolyte (3 mmol), solvent (1:1, 50 mL), 3 hours. ^bYield refers to isolated yield. ^c82% yield was obtained after 12 hours. ^dPartial conversion even after 12 hours.

To optimize the reaction conditions such as concentration of azide, type of solvents, solvent to water ratio and applied voltage, and to investigate the role of sodium ascorbate, one of the azide (tosyl azide) was subjected to electroreduction. The results are tabulated in Table 1. It was observed that no reaction took place in the absence of electrolytes. It may be due to the poor conductance of the medium which is an inevitable condition for the smooth electron transfer process. A moderate or poor yield of the sulphonamides was obtained in the presence of NaCl and tBuN+Br-. But a very good percentage of the expected product was noted in the presence of ascorbate. It can be assumed that sodium ascorbate played a dual role in the electrochemical reduction process. It can act both as an electron transferring agent from the cathode to the azide and a supporting electrolyte which can enhance the conductance of the medium. Methanol-water mixture (1:1) was the most suitable medium for the electrochemical reduction. In the presence of chloroform-water mixture only 15% yield was noticed.

Applied potential showed a linear relationship with the yield of sulphonamide up to 20 V and remained constant after this. The variation of applied potential against the percentage of the product is shown in Fig. 2. It is also observed that the reaction attained >80% completion when the time was increased from 3 to 12 h at a constant potential of 10 V.

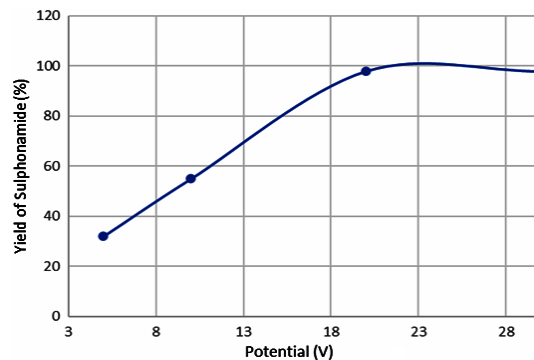


Fig. 2. Variation of applied potential against the yield of sulphonamide at 3 hours

Initially, the studies were performed with readily available sulphonyl azides. Also, sulphonyl azides were prepared by treating sulphonyl chloride with NaN₃ following the reported procedure.¹⁶ Thus obtained sulphonyl azides were subjected to reduction without further purification. The sulphonyl azides were electrochemically reduced to get the corresponding sulphonamides in excellent yields. During the reaction, there was gradual increase in the temperature of reaction mixture and it reached 52°C after 3 h of the reaction time. The sulphonamides obtained as colourless solid was pure enough to record the spectral data without purification. The compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR and by comparing melting points. (All compounds were previously reported. We have compared the spectral data of sulphonamides and amines with that of previously reported compounds and found in good agreement. Then attempts were made to reduce aryl and alkyl azides under the same condition. The reaction was sluggish and gave the corresponding amines in moderate yields. The lesser reactivity of aryl azide is attributed to the electron richness of the azide group. In sulphonyl azides, N₃ is attached with electron withdrawing SO₂ which decreases the electron density considerably and facilitate the electron transfer and thereby the reduction. The detailed structures of the reactant azides and products with the yield are depicted in Table 2.

Table 2: Electrochemical reduction of azidea

Sr. No	Reactant	Product	% Yield
1			93e
2			98e
3			95e
4			95e
5			99c
6			56d
7			61
8			58
9			65d
10			68

^areaction condition: Azide (3 mmol), Sodium ascorbate (3 mmol), EtOH:H₂O (1:1,50 mL), Pt electrode, 30 V (A), 3 hours. ^bThe yields refer to the isolated yield after column purification. ^cRefers to conversion as measured by HPLC. ^dThe compounds were characterized and confirmed by liquid chromatography techniques. ^eThe compounds were crystallized in MeOH and melting points were recorded

As the reaction failed to proceed in the absence of the sodium ascorbate, attention was made to explore the involvement of ascorbate. The role of sodium ascorbate in the CuSO₄ catalyzed cycloaddition between azide and alkyne is to reduce the Cu(II) to active Cu(I) by giving one electron.¹⁷ The free radical formed after the electron donation is stabilized by resonance and found to be quite stable (Fig. 3). Similarly, in this reaction, the role of sodium ascorbate is believed to donate electron to the sulphonyl azide. Since azide nitrogen atoms are relatively electron rich, electron cannot be given readily to them and the reduction is less facile. So it is presumed that sodium ascorbate serve as mediator in the electron transfer (Fig. 3). Considering the structure of azide (R-N=N+=N-) it is clear that the azide nitrogen atoms are highly electron rich and carry lone pair of electron or -ve charge. The central nitrogen atom carries +ve charge and electron cannot be given to

central N atom, as the valency of nitrogen cannot be five. Also, sodium ascorbate acts as the electrolyte in the reaction and no other electrolyte is required. In a control experiment, the reaction was carried out in the absence of sodium ascorbate and the reaction failed to give the desired product.

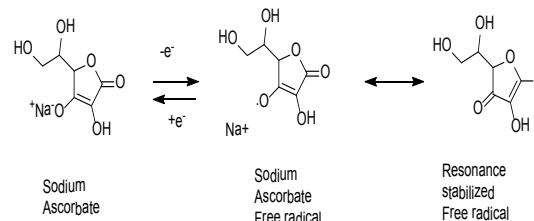


Fig. 3. Stabilisation of ascorbate ion

Cyclic voltametric studies

To understand the electrochemical behaviour of the reaction, cyclic voltametric studies were performed on the reactants and the reaction mixture. Fig. 4 represents the overlay voltammograms of sodium ascorbate, tosyl azide and the reaction mixture (TsN₃, Sodium ascorbate in methanol:H₂O) at a scan rate 50mV/s. The voltammogram of the ascorbate was smooth and no significant reduction/oxidation peak was noticed in the 0-2 V scan range. The poor electrochemical response of sodium ascorbate suggests that none of the functional groups present in the molecule get oxidized or reduced. Similarly, sulphonyl azide didn't exhibit any redox peaks in the voltammogram. It is evident from the figure (Fig. 5) that the reaction mixture displayed appreciable electrochemical response in the cyclic voltametric analysis. The loop 'c' corresponds to the reaction mixture and indicates the electrochemical nature of the product formed. The sulphonamide generated didn't show any well-defined reduction peak during the scan. But a clear oxidation peak was observed at 1.22 V in the CV plot which may be attributed to the oxidation of the -NH₂ group present in the sulphonamide.

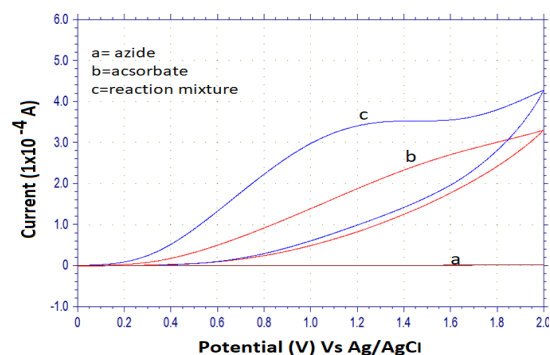


Fig. 4. Cyclic voltammograms of reactants and reaction mixture

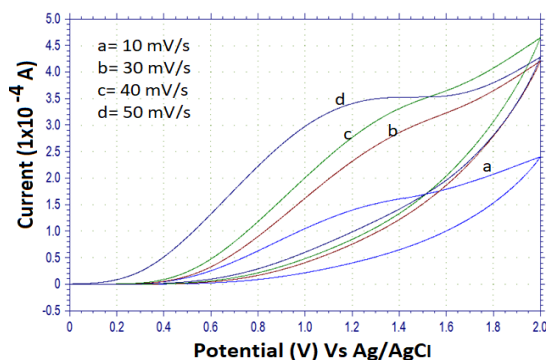
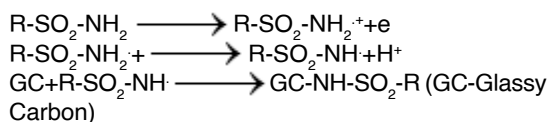


Fig. 5. CV plots of reaction mixture at various scan rates

The mechanism of the electrochemical process taking place during cyclic voltametric analysis can be explained as follows:¹⁸



Cyclic voltametric data and the corresponding CV plots of the sulphonamide at various scan rates are given in Table 3 and Fig. 5 respectively. As the scan rate increased, the oxidation peak of the reaction mixture moved to less positive potential side and the magnitude of the anodic peak current increased as displayed in the CV plot. It can be assumed that the easiness of the oxidation is enhanced at high scan rates compared to low scan rates.

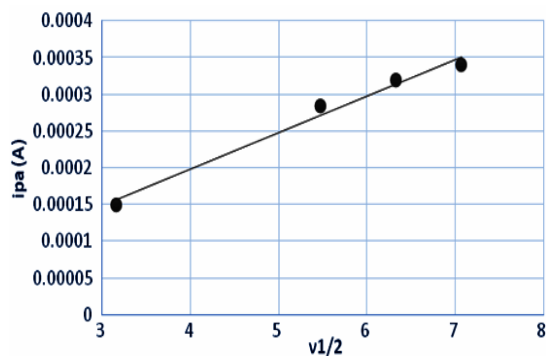


Fig. 6. i_p - $v^{1/2}$ curve of the reaction mixture

Table 3: Cyclic voltametric data of the reaction mixture at different scan rates

Scan rate (v) mV/s	V	(v) ^{1/2}	Current ip(mA)
10	1.5	3.162278	0.15
30	1.36	5.477226	0.284
40	1.33	6.324555	0.32
50	1.22	7.071068	0.34

Figure 6 represents the i_p - $v^{1/2}$ curve of the reaction product with sodium ascorbate in methanol. As seen from the plot, the peak current obtained at different scan rates were found to change linearly with the square root of the scan rate, confirms that the rate of oxidation of the sulphonamide molecule on the glassy electrode surface follows diffusion controlled electrochemical process.

Mechanism

Mechanistically, it is believed that the sodium ascorbate gives electron to the azide nitrogen to give radical. Sodium ascorbate radical is converted back to sodium ascorbate by taking one electron from applied current (Fig. 7). In the absence of applied current, there is no reduction of azide even if stoichiometric amount of sodium ascorbate is employed. Also, no reaction took place in the absence of sodium ascorbate. This leads to the conclusion that the transfer of electron from the sodium ascorbate is facilitated in the presence of electron source i.e applied current. Thus, formed azide radical further takes electron to give anion and decomposes to amine, liberating N_2 gas.

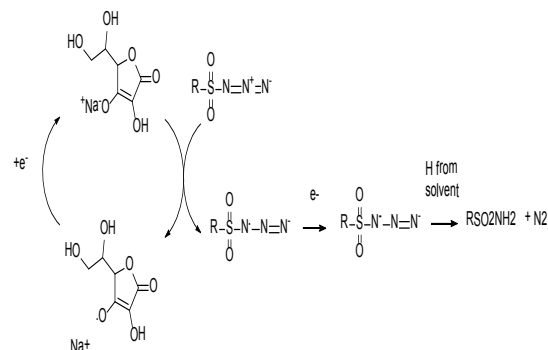


Fig. 7. Plausible reaction mechanism

CONCLUSION

In this work we developed a facile, green and economic electrochemical method to reduce organo azides to the corresponding amine or sulphonamide using sodium ascorbate as the promoter. An external potential of 30 V was employed for the electrochemical process with platinum electrodes. The obtained products were highly pure and characterized using NMR and FT-IR spectroscopic techniques and melting point determinations. Moderate to high yield of the products were noted. Cyclic voltametric studies were conducted to explain the electrochemical response

of the reaction mixture and the reactants.

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