Electrochemical synthesis of aromatic hydroxylamines and amines and its comparison with chemical synthesis

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Manuscript received 3 November 2004, revised 19 May 2005, accepted 2 July 2005

The electrochemical studies on the reduction of some aromatic compounds viz. nitrobenzene, m-nitrobenzoic acid, m-dinitrobenzene and p-N,N-dimethylamino-benzaldehyde-2,4-dinitrophenylhydrazone is being reported here. Constant potential electrolysis was carried out using 1 cm × 0.5 cm Pt plates as working and counter electrodes. In all the reactions amines are obtained as final product after reduction.

In the present communication the electrochemical synthesis of hydroxylamines and amines were carried out at controlled potential in weakly acidic medium. This synthetic procedure consists of reduction of aromatic nitro compounds viz. nitrobenzene, m-nitrobenzoic acid, m-dinitrobenzene and p-N,N-dimethylamino-benzaldehyde-2,4-dinitrophenylhydrazone. At definite potential the electrode surface is covered by a layer of the product which is continually diffused in the bulk and is visible with naked eyes.

Results and discussion

The nitro group readily undergoes reduction in protic as well as in aprotic solvents. Similar to carbonyl group, the electrochemical reduction of nitroaromatics in aprotic system takes place through the stable anion radicals. Although the reduction of carbonyl group have been carried out in aqueous medium, in the electrochemical reduction of nitro compounds we used DMF as a solvent and an electrolyte in the presence of a proton donor (especially a weak acid is only required). Even phenol (pKa = 9.98) which is a very weak acid can act as a proton donor. Even phenol (pKa = 9.98) which is a very weak acid can act as a proton donor. In this system the nitro compound is first reduced to nitroso compound and then the nitroso group is reduced into hydroxylamine and amines simultaneously at room temperature at a very low potential range 1.2–2.00 V. The electrochemical behaviour of nitro compounds is greatly influenced by inductive and resonance interactions and by intramolecular reactions of electrogenerated intermediates with substituents present in the molecule.

The mechanism of the reaction described in a series of steps involving protonation with electron transfer. The whole reaction steps are represented in the form of single equation as:

\[
\text{C}_6\text{H}_5\text{NO}_2^{4e^-}, 4\text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{NHOH}^{2e^-}, 2\text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{NH}_2
\]

All the electrolysis was carried out at their corresponding reduction potentials and were completed in 2 h (Table 1). After 2 h no reduction product was seen to diffuse in the bulk.

The products are extracted from non-aqueous solution [dimethylformamide (DMF) and dimethylsulfoxide (DMSO)] with double distilled water. All the products except phenylenediamine, which was a light colour needle like shining crystalline solid, were dark coloured and entirely different from those of starting material. The product of nitrobenzene was an oily liquid.

It is obvious from the studies that the reduction of nitroaromatics provides a good method of electroorganic synthesis of amines. The reduction of nitro group gives hydroxylamines and finally amines in the presence of weakly acidic medium provided by the phenol. The nitro functional group undergoes reduction in protic as well as in aprotic solvents.

Here the synthesis of hydroxylamines and amines involve both platinum electrodes as working as well as counter electrode, a small amount (5 mL) of phenol and DMF as solvent for reactant. The reaction takes place at room temperature and there is no danger in the handling of reagents in this process.

Approximately the same mechanistic pathway and same product is obtained by chemical reduction of nitrobenzene and other compounds on reduction with iron or tin in hydrochloric acid. Although hydrochloric acid is stronger acid in comparison to phenol, the reduction of ni-
Note

| Sl. no. | Reactant                  | Time (h) | Applied potential (mV) | Current (mA) | Yield (%) |
|--------|---------------------------|----------|------------------------|--------------|-----------|
| 1.     | Nitrobenzene              | 2        | 1960                   | 0.96–0.25    | ≥60       |
| 2.     | m-Nitrobenzoic acid       | 2        | 1970                   | 0.36–0.18    | ≥10       |
| 3.     | m-Dinitrobenzene          | 2        | 1450                   | 0.15–0.09    | ≥55       |
| 4.     | Schiff base               | 2        | 1500                   | 0.03–0.02    | ≥55       |
| 5.     | Schiff base               | 2        | 1500                   | 0.03–0.02    | ≥55       |

| (DMF)  | (DMSO)                    |           |                        |              |

The chemical reduction of nitrobenzene in neutral medium with Zn dust and NH₄Cl solution gives phenylhydroxylamine. The phenylhydroxylamine can also be obtained by electrochemical reduction of nitrobenzene, by using a very weak acid such as phenol, but the chemical reduction requires a variety of chemicals, which can be hazardous to environment and also the product obtained by chemical reduction method is not in pure state.

On the basis of above merits it is concluded that our electrochemical method for the synthesis of amines and hydroxylamines from their nitro derivatives is simple and ecofriendly synthetic method and hence a part of green chemistry.

All the products are analysed by chemical methods as well as by spectral methods.

As per mechanism following products are formed,

$$C₆H₅NO₂ \rightarrow C₆H₅NHOH \rightarrow C₆H₅NH₂$$

$$\text{HOOC-C₆H₄NO₂} \rightarrow \text{HOOC-C₆H₄NH₂}$$

$$O₂N₆C₆H₄NO₂ \rightarrow H₂N₆C₆H₄NH₂$$

$$(\text{CH}_3)₂NC₆H₄CH=NNHC₆H₄(NO₂)₂ \rightarrow (\text{CH}_3)₂NC₆H₄CH=NNHC₆H₄(NH₂)₂$$

The starting material shows positive test of nitro group, whereas products are not responding the test of nitro group with the same reagent.

The IR spectra of the products showed characteristic IR band at 3276.9, 3249.8 and 3416.1 cm⁻¹ corresponding to the product aniline, m-hydroxylaminobenzoic acid and phenylenediamine formed from the nitrobenzene, m-nitrobenzoic acid and m-dinitrobenzene respectively. The sharp bands at 3275.7 and 3414.1 cm⁻¹ in the product p-N,N-dimethylnitrobenzaldehyde-2,4-dinitropheny hydrazone suggest complete reduction of -NO₂ group in -NH₂ group.

**Experimental**

**Reaction mixture:** The reaction mixture contains 50 mL of the solution of starting material using dimethylformamide as aprotic solvent (strength of the solution is given in the table), 50 mL of the 0.1 N aqueous solution of KCl and 5 mL of phenol (pKa = 9.98) which serves as a proton donor. Starting materials (strength 4% w/v) were, nitrobenzene, m-nitrobenzoic acid and m-dinitrobenzene and the Schiff base was a self synthesised compound. Water used was double distilled. All other reagents were analar quality.

The electrolysis were carried out at constant potential in four necked 250 mL flask. For constant potential electrolysis, we have used conventional three electrode cell assembly with platinum (flattened sheet of dimension 1 cm × 0.5 cm) as working as well as counter electrode. These Pt-electrodes are surrounded from one side with glass material and saturated calomel electrode (SCE) is used as reference electrode.

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