



SYNTHESIS AND ELECTROCHEMICAL STUDIES OF 3-HYDROXY-3-PHENYL-1-P-SULFONATO (SODIUM SALT) PHENYLTRIAZENE

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ABSTRACT

The compound 3-hydroxy-3-phenyl-1-p-sulfonato (sodium salt) phenyltriazene (HPSPT) has been synthesized using standard method i.e. by preparing hydroxylamine from nitrobenzene, diazotization of sulphanilic acid and subsequently coupling them at 0-5°C. Compound is yellow crystalline solid having m.p. 157°C. It has been reduced at dropping mercury electrode using universal buffer. Compound gives well defined Polarographic waves between pH 4.5 to 6.5. A mechanism of reduction has been proposed indicating a six electrons reduction corroborating the earlier studies on similar compound.

Keywords: 3-hydroxy-3-phenyl-1-p-sulfonato (sodium salt) phenyltriazene, Polarographic reduction.

INTRODUCTION

Hydroxytriazenes are well known chelating agents as revealed by reviews appearing on them during last few years¹⁻⁷. Although the ligands have been studied in details as spectrophotometric reagents, hardly any attempt has been made on the electrochemical behaviour of these ligands. Even their electrochemical studies as ligands with transition metals are of recent origin. Since the electrochemical behaviour of electron transfer processes are similar to biological processes, and number of hydroxytriazenes and their metal complexes have shown excellent biological activities⁸⁻¹³. In view of this the present studies have been undertaken for water soluble HPSPT at d.m.e in universal buffer (pH 2 to 12).

EXPERIMENTAL

HPSPT has been synthesized as described here. In this method nitrobenzene (12.3 ml) was reduced with Zn dust (20 g) in the presence of NH₄Cl (5.3 g) at 40-60°C to obtain phenyl hydroxylamine. The diazotized product was obtained by adding sodium nitrite (6.9 g) to sulphanilic acid (17.3 g) dissolved in 20 ml HCl and 100 ml water in small lots at 0-5°C under constant mechanical stirring. The diazonium compound was coupled with phenyl hydroxylamine at 0-5°C under mechanical stirring with occasional addition of sodium acetate solution for maintaining pH close to 5 during coupling process. After complete addition of diazonium salt NaCl was added in sufficient quantity for salting out. The hydroxytriazene was obtained as yellowish brown micro crystals after crystallization from double distilled water. Its purity was checked by m.p. determination and CHN analysis. M.P. was found 157°C. The theoretical and experimental values of %C, %N and %H were obtained 43.2, 12.6, 3.6 and 42.4, 12.6, 3.6 respectively.

Further the compound was subjected to IR spectral analysis which yielded the characteristics bands reported for hydroxytriazenes⁵ and their values for ν_{O-H} , ν_{N-H} , δ_{N-H} and δ_{N-OH} are 3450, 3190, 1590 and 940 respectively. The IR spectra confirmed their presence establishing purity of compound.

A systronics polarograph 1632 was used for obtaining C.V. curves. The electro-chemical behaviour of HPSPT was studied polarographically in aqueous medium on d.m.e., at different pH values using citric

acid and Na₂HPO₄ buffer solution as supporting electrolyte. All the experiments were performed at room temperature. The solutions were deoxygenated by purging high purity nitrogen gas for at least 15 minutes before taking measurement. The drop time was 1 sec. diffusion controlled nature of each wave was verified by i_d vs. C and i_d Vs \sqrt{h} plots. Gelatin was used as maximum suppressor. Ionic strength was kept constant by using KCl.

RESULTS AND DISCUSSION

In all the cases in Table-1 where the electrochemical reduction was studied (in the pH range 4.5 to 6.5) a well defined single wave was obtained. The slope analysis indicated a six electron irreversible reduction method.

In organic compounds the depolarizer species is initially protonated followed by electron transfer. Thus, the protonation decides ease or difficulty in the reduction process. The experimental results corroborate the fact i.e. between pH 2.5 to 9.5 consequently the protonation of depolarizer decreases and thus the reduction occurs at higher negative potential.

Thus, in the present study, it is proposed that the compound HPSPT is reduced to phenyl hydrazine and sodium 4-aminobenzene sulfonate through six electrons irreversible reduction mechanism. Further, in the basis of product analysis using thin layer chromatography, it is further supported since a single spot for amino compound which is the end product, is obtained. The final product was also tested qualitatively for amino group which proves the proposed mechanism. A similar mechanism has been proposed for 1, 3-diphenyl-3-hydroxytriazene, by Verma *et.al*¹⁴ using cyclic voltametry.

The proposed mechanism is corroborated by the fact that reaction shown in Scheme-1 and Scheme-2 involve all the steps at the same potential and hence a single reduction peak involving transfer of six electrons is obtained. The same fact has been verified by Verma *et al.* through product analysis. Thus, in our case compound HPSPT is reduced polarographically between pH 2.5 to 9.5 producing aniline and phenyl hydrazine as product.

Thus, the present studies propose electrochemical reduction of hydroxytriazenes at d.m.e.

CONCLUSIONS

3-hydroxy-3-phenyl-1-p-sulfonato (Sodium salt) phenyltriazene reduces electrochemically, to phenyl hydrazine and sodium 4-aminobenzenesulfonate through six electrons irreversible reduction mechanism.

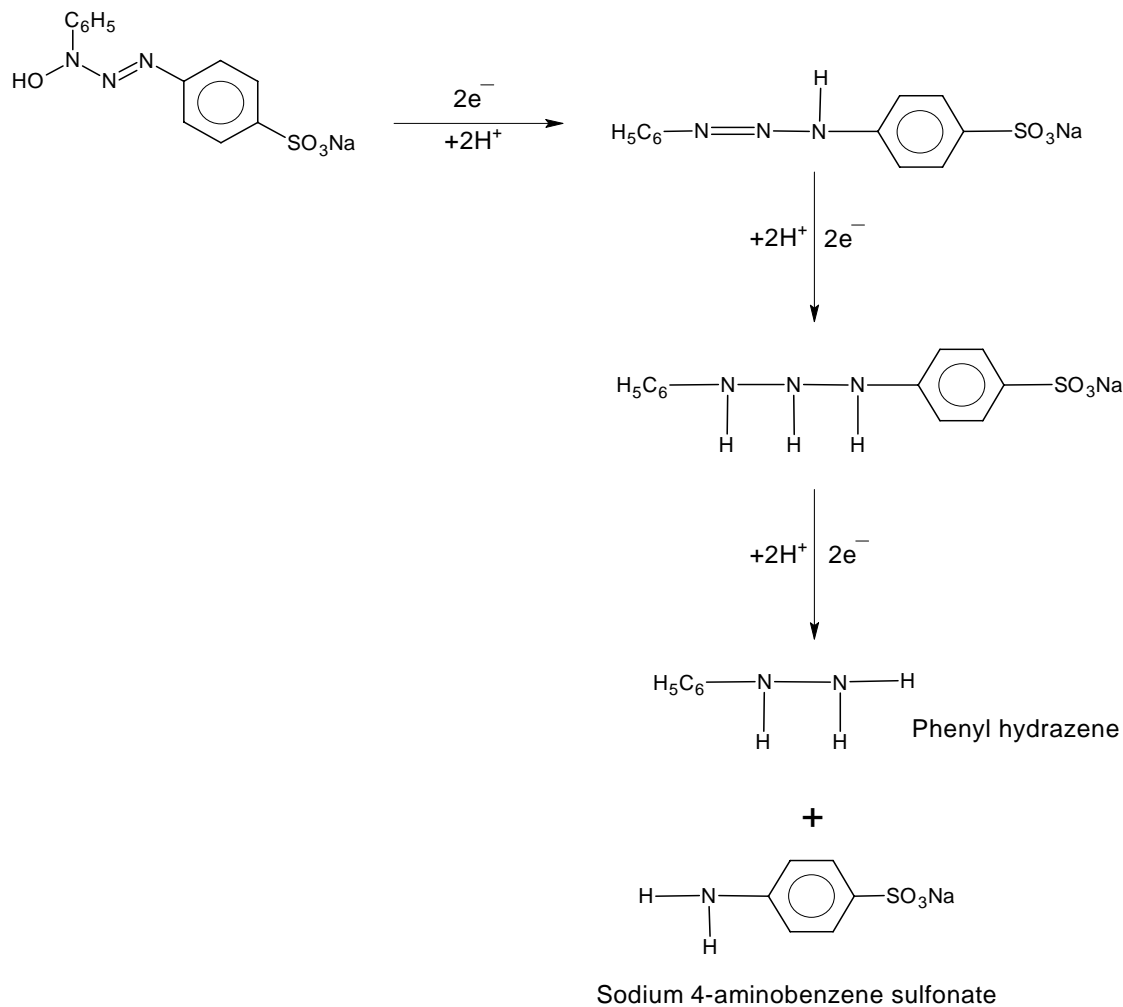
Table-1: Dependence of $E_{\frac{1}{2}}$ and i_d on pH of 3-hydroxy-3-phenyl-1-p-sulfonato (sodium salt) phenyltriazene

S.No.	pH	i_d (μ A)	$E_{\frac{1}{2}}$ (-V Vs SCE)
1	2.5	170	.920
2	3.5	160	.940
3	4.5	200	.960
4	5.5	210	1.030
5	6.0	320	1.035
6	6.5	340	1.060
7	7.0	420	1.065
8	8.0	380	1.100
9	9.5	385	1.120

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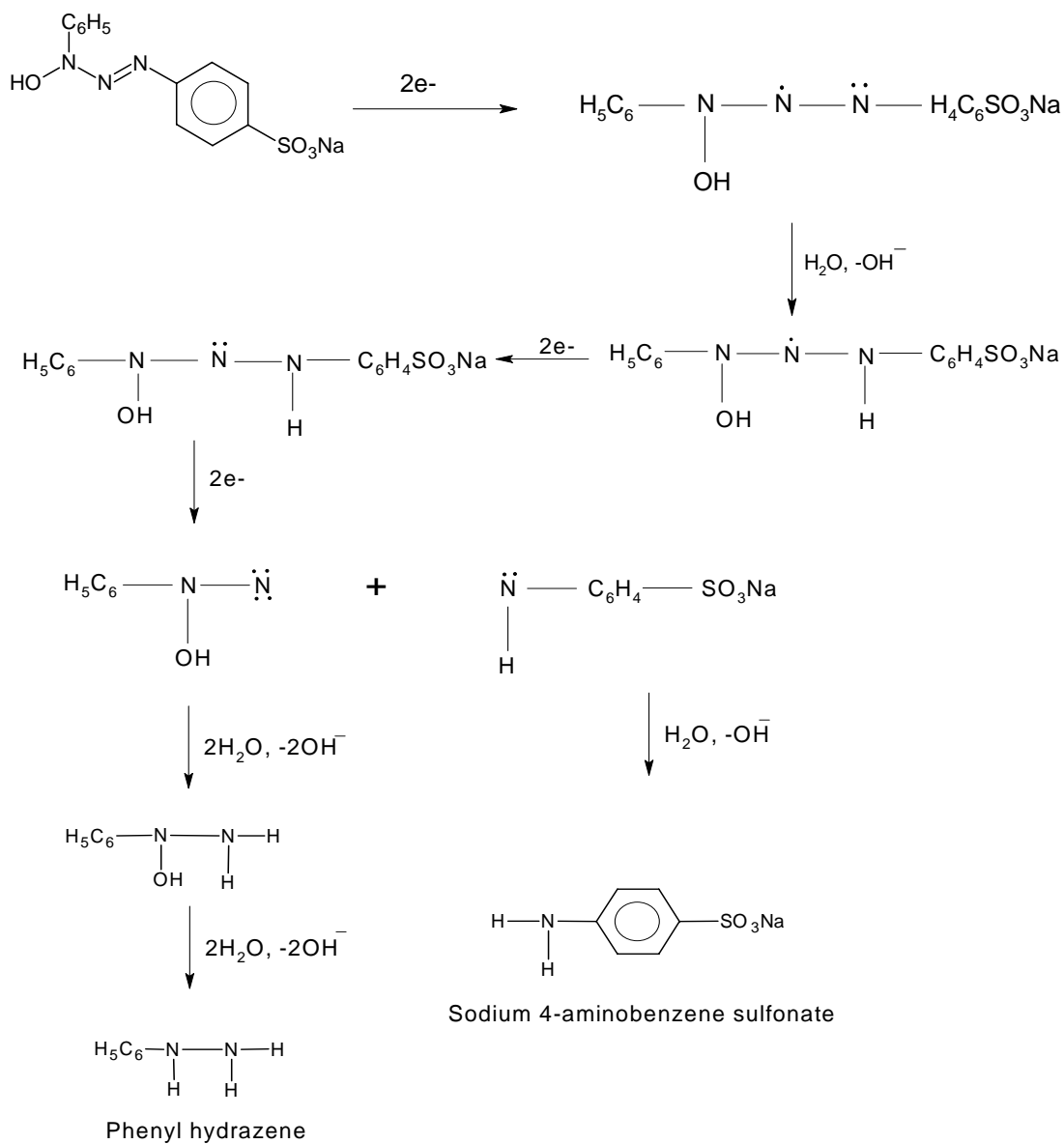
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Scheme -1: In the acidic pH the mechanism takes following steps.

In alkaline medium



Scheme-2: In the basic pH the mechanism takes following steps:

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