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SYNTHESIS AND ELECTROCHEMICAL STUDIES OF 3-HYDROXY-3-m-TOLYL-1-p-(SULPHONAMIDO) PHENYLTRIAZENE

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ABSTRACT

The compound 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido) phenyltriazene has been synthesized and reduced at dropping mercury electrode using universal buffer as medium between 7.5 to 9.5. Well defined polarographic waves are obtained having diffusion controlled nature. This is first attempt to study electrochemical behaviour of some hydroxytriazenes, which are promising bioactive compounds.

Keywords: m-Nitrotoluene, Hyroxytriazene, Polarography, Electrochemical studies**.**

INTRODUCTION

Hydroxytriazene are well established chelating agents as revealed by reviews appearing on them during last few years[1-7]. These compounds have been used as spectrophotometric and complexometric reagents for determination of transition and non-transition elements[8-10]. However, there are hardly any studies on the polarographic behavior of these ligands. Since the electrochemical processes are similar to biological processes and number of hydroxytriazenes and their metal complexes have shown good biological activities[11-15], such studies would help to understand their mechanism in biological systems. In view of this the present studies have been undertaken 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido)phenyltriazene at d.m.e in universal buffer (pH 2 to 12).

EXPERIMENTAL

Synthesis of 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido) phenyltriazene

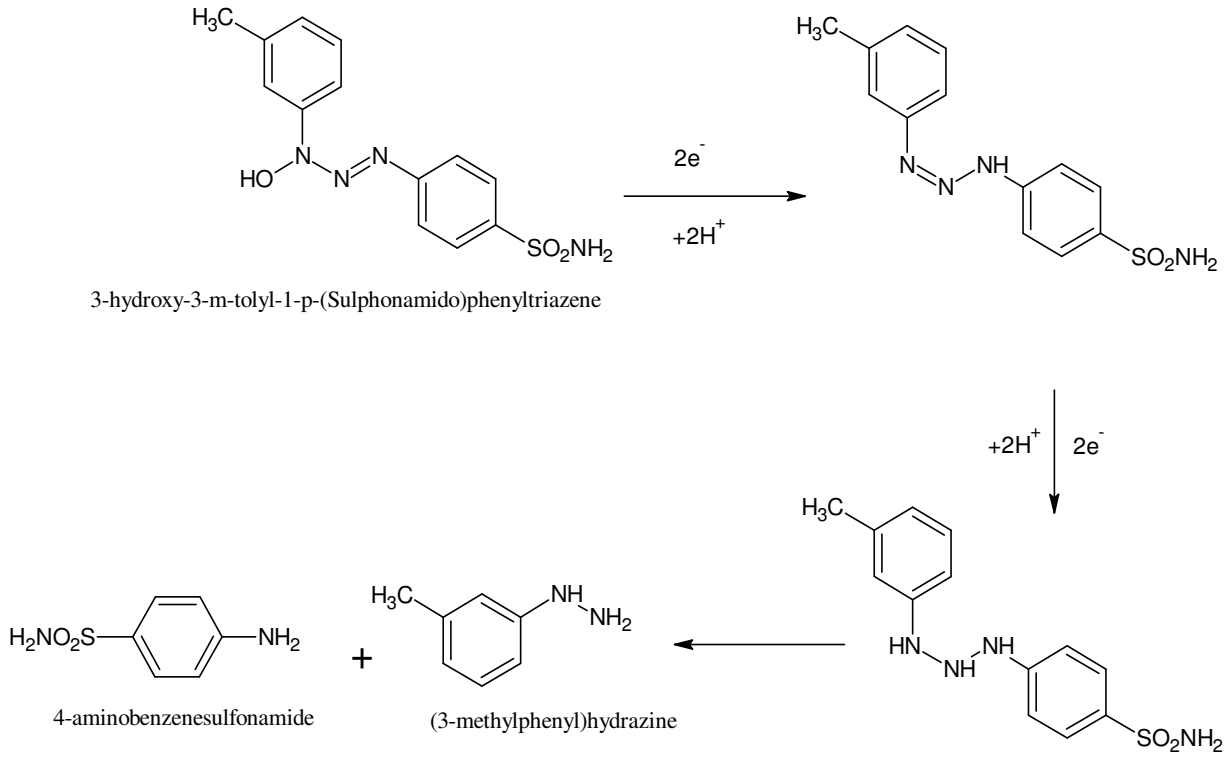
Synthesis of m-tolyl-hydroxylamine: In a one litre beaker (0.1 mol) of m-nitrotoluene, 5 gm of NH_4Cl 50 ml water and 50 ml C_2H_5OH were mixed, stirred mechanically and cooled to 0° C by surrounding the beaker with ice salt mixture, 20 gm Zn dust was added in small lots such that the temperature of reaction mixture remained between 0 to 5° C. Addition of Zn dust was completed in 40 min. The reaction mixture was stirred mechanically for another 15 min. The solution was filtered under suction and washed with ice cold water. The filtrate was taken in a beaker and kept in freezer and used as such for coupling with diazotized product. Diazonium salt of sulphanilamide: In a 500 ml beaker 0.1 mol (17.2 mL) of sulphanilamide was dissolved in warm mixture of 25 mL of concentrated HCl and 25 mL of water. After constant stirring the mixture was kept in a freezer to cool. In another beaker 6.9g of $NaNO_2$ was dissolved in 20 mL of distilled water and kept it in the freezer. The beaker which contained sulphanilamide solution was put in an ice bath to maintain temperature between 0 to 5º C. To this The $NaNO_2$ solution was added drop by drop with continuous stirring. The diazotized product so obtained was directly used for coupling.

Coupling of m-tolyl-hydroxylamine with diazonium salt of sulphanilamide:

The m-tolylhydroxylamine prepared in step (a) was coupled with the diazotized product of (b) step at 0 to 5°C under mechanical stirring with occasional addition of sodium acetate solution for maintaining the pH close to 5 during coupling process. The compound was 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido)phenyltriazene obtained as yellowish fluffy powder after crystallization from ethanol.

Melting points of all synthesized compounds were taken in open capillaries and are uncorrected. C H N analysis corroborated the purity of compound. the compound was subjected to IR spectral analysis and following bands were observed.

IR (KBr) cm^{-1}: 3249 (O-H str.), 3078 (C-H str. Ar), 2981 (C-H str., CH_3), 1632 (N=N str.), 1419 (N-N str.).The spectra showed the compound to be in pure state. IR spectra (KBr) were recorded on FT IR RX1 Perkin Elmer Spectrometer. A Systronics Polarograph 1632 was used for obtaining current voltage curves. Physical and analytical data are given in Table-1**.**



Scheme-1

Polarographic study of 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido)phenyltriazene:

The electro-chemical behavior of 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido) phenyltriazene was studied polarographically in the mixture of acetone and water on d.m.e., at different pH values using citric acid and Na_2HPO_4 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 min. before taking measurements. Diffusion controlled nature of each wave was verified by id Vs C and id Vs √h plots. Triton-X-100 was used as maximum suppressor. Ionic strength was kept constant by using KCI. The capillary had following characteristics t =1 drop/sec, m =1.35 mg/sec. IR drop correction were applied.

RESULTS AND DISCUSSION

In all the cases where the electrochemical reduction was studied (in the pH range 2.5 to 9.5) 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 decrease and thus the reduction occurs at higher negative potential and all data given in Table-2, which has been observed in

case of this compound. In views of this mechanism of reduction for the compound 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido) phenyltriazene has given in Scheme-1 and 2..

The proposed mechanism is corroborated by the fact that above reaction involves 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[16]. Thus in our case compound 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido) phenyltriazene is reduced polarographically between pH 2.5 to 9.5 producing aniline and phenylhydrazine as product. Thus the present studies propose electrochemical reduction of hydroxytriazene at d.m.e.

In the acidic pH the mechanism takes following steps (Scheme-1) and in the basic pH the mechanism takes following steps (Scheme-2).

Table-1:Elemental analysis of 3-hydroxy-3-m-tolyl-1-p-(Sulphonamido) phenyltriazene

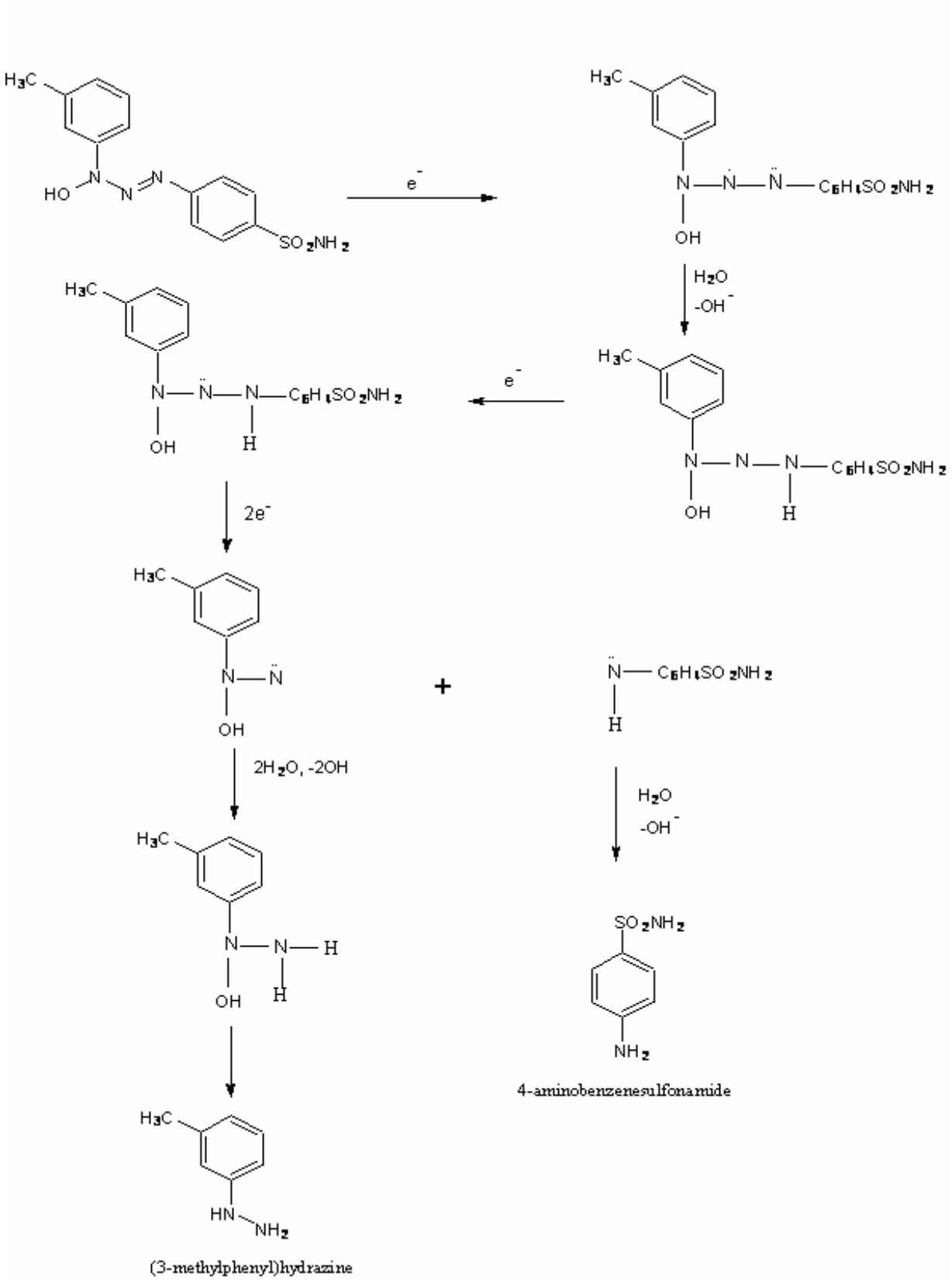
Comp	Mol. Formula	Mol. Weight	M.P. ºC	Yield %	Found/(calculated)		
					C %	N%	H%
1	($C_{13}H_{14}N_4O_3$.S)	306	188 ºC	79	50.944 8.95	4.57 4.61	18.21 8.7

Table-2: Dependence of $E_{1/2}$ and id on pH of 3-hydroxy-3-m-tolyl-1-p- (Sulphonamido) phenyltriazene

S.No.	pH	id (µA)	$E_{½}$ (V Vs SCE)
1	2.5	172	0.998
2	3.5	167	1.094
3	4.5	202	1.103
4	5.5	212	1.109
5	6.5	317	1.113
6	7.5	342	1.333
7	8.5	412	1.393
8	9.5	392	1.403

CONCLUSION

3-hydroxy-3-m-tolyl-1-p-(Sulphonamido)phenyltriazene reduces electrochemically, to (3-methylphenyl)hydrazine and sodium 4-aminobenzenesulfonamide through six electrons irreversible reduction mechanism.


e⁻
H₂O
-OH⁻
e⁻
2e⁻
2H₂O, -2OH
+
H₂O
-OH⁻
4-aminobenzenesulfonamide
(3-methylphenyl)hydrazine

Scheme-2

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