Asian Journal of Chemistry Vol. 22, No. 4 (2010), 2599-2605

Electrochemical Behaviour of 3-Ethyl-1-phenyl-3-hydroxytriazene

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3-Ethyl-1-phenyl-3-hydroxytriazene (EPHT) was synthesized, purified and characterized by elemental analysis and spectral studies. Electrochemical reduction of EPHT has been studied at various scan rates at glassy carbon electrode (GCE) and platinum electrode by cyclic voltammetry. The kinetic parameters have been evaluated. 3-Ethyl-1-phenyl-3-hydroxytriazene reduction appears to involve irreversible electron transfer in the potential range 800-1500 mV *vs.* Ag, AgCl. Controlled current electrolysis of EPHT was also carried out using stainless steel (SS-316) electrodes. The proposed mechanism of the reduction is discussed in acidic, neutral and basic media.

Key Words: 3-Ethyl-1-phenyl-3-hydroxytriazene, Stainless steel (SS-316) electrode, Cyclic voltammetry.

INTRODUCTION

Hydroxytriazenes are widely used as ligand to coordinate various transition or inner transion metal ions due to their good solubility in common solvents and the high stability of their complexes. These compounds have a variety of application in gravimetric and spectrophotometric determination[1-4] of transition metal ions such as Pd, Cu, Ni, Fe, *etc.*

The present communication deals with the synthesis, spectral and electrochemical studies of 3-ethyl-1-phenyl-3-hydroxytriazene (EPHT). The electrochemical reduction of EPHT has been studied over a wide range of pH at glassy carbon electrode in aqueous methanolic medium and at platinum electrode in CH_2Cl_2 by cyclic voltammetry. Then it was reduced galvanostatically at constant current using stainless steel (SS-316) electrodes being less expensive and easily available[5,6].

EXPERIMENTAL

All the chemicals and solvents used in synthesis and electrochemical measurements were of A.R. grade. The solvents used were methanol and dichloromethane. sodium perchlorate and tetraethyl ammonium perchlorate were used as supporting electrolyte. A series of Britton-Robinson buffer solutions of different pH values ranging from 5.0-9.0 were prepared and used to maintain the pH of the examined solution.

Synthesis of 3-ethyl-1-phenyl-3-hydroxytriazene: 3-Ethyl-1-phenyl-3-hydroxytriazene was synthesized by reacting ethyl hydroxylamine with benzene diazonium chloride at 0-5 ºC in 1:1 molar proportion using sodium acetate buffer (pH = 5.00) as reported in the literature[7]. It was recrystallized using aqueous-alcoholic mixture to yield light yellow needle shaped crystals. Further its purity was also confirmed by thin layer chromatography.

3-Ethyl-1-phenyl-3-hydroxytriazene was characterized by elemental analysis and spectral studies. IR spectra were recorded using FTIR spectrophotometer (model 8400S, Shimadzu) in KBr wafer and ^{1}H NMR spectra were recorded on 300.4 MHz FT-NMR spectrometer (model Jeol AL 300) in $CDCl_3$ using TMS as an internal standard.

The electrochemical behaviour of EPHT was studied cyclic voltammetrically in aqueous methanolic medium on glassy carbon electrode at different pH values, *viz.* 5.0, 7.0 and 9.0 using sodium perchlorate as supporting electrolyte. Britton-Robinson series buffer solutions were used to maintain the pH of the solutions. Cyclic voltammograms of EPHT were also recorded in dichloromethane at Pt electrode using tetraethyl ammonium perchlorate as supporting electrolyte. All cyclic voltammograms were recorded on a fully computer controlled basic electrochemistry system (model ECDA 001) using a one compartment three electrode system, in which 1 mm diameter glassy carbon/Pt electrode were used as working electrode, Ag/AgCl as reference and Pt wire as an auxiliary electrode. The working electrodes were polished with Al_2O_3 suspension prior to every experiment. All the experiments were performed at various scan rates at room temperature 25 ± 0.5 °C. Before voltammetric measurements, the solutions were purged with nitrogen for 20 min to remove dissolved oxygen and a stream of nitrogen gas was flushed over the solution.

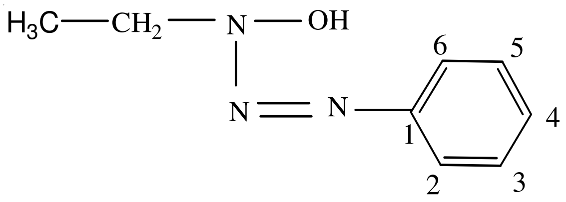
Controlled current electrolysis of EPHT was carried out at 0.5 amp for 24 h in aqueous methanolic solution (1:1, v:v) employing galvanostat assembled by Center for Development of Physics Education, University of Rajasthan, Jaipur, India. The solution of EPHT (0.01 M) containing 1 M CH_3COONa was taken in a two compartment H-shaped glass cell provided with a fritz glass disc (G-3) and was stirred using hot plate cum stirrer (Remi model 2 LH). Stainless steel (SS-316) electrodes of size $4\ cm^2 \times 4\ cm^2$ were used as cathode as well as anode. The volume of catholyte was reduced by distilling at reduced pressure. The products obtained after repeated extraction with diethyl ether were purified and characterized by combined applications of chromatography and spectral studies.

RESULTS AND DISCUSSION

Spectroscopic techniques were used to elucidate the structure of EPHT. The IR spectrum of EPHT displays absorption bands at 3280 cm^{-1} [ν(O-H)], 1300 cm^{-1} [δ(O-H)], 1530, 1500 and 1440 cm^{-1} [ν(C=C) in plane skeletal vibrations], 1380 cm^{-1} [ν(N=N)], 985 cm^{-1} [ν(N-O)], 1260 cm^{-1}, 1160 cm^{-1} [δ(C-H) in-plane], 1030 cm^{-1} and 690 cm^{-1} [δ(C-H) out-of-plane].

The ^{1}H NMR spectrum of EPHT shows signals at δ 2.0, δ 2.5 ethyl protons, δ 6.99 aryl protons and at δ 9.8 OH proton.

All the spectroscopic results are in confirmity with the reported literature values and structure[8].



The cyclic voltammograms of EPHT were recorded with an initial potential (E_i) between 800-1000 mV and switching potential (E_s)-1500 mV at different scan rates 50, 100, 200, 500 mV/s. in aqueous methanolic solutions. Figs. 1-3 represents the cyclic voltamograms of EPHT recorded at a concentration of 0.16 × 10^{-3} mol dm^{-3} at glassy carbon electrode. All the voltammograms showed only one peak in the cathodic region. Absence of the anodic wave in the reverse scan indicates the irreversible nature of the electron transfer process. The irreversibility of the electrode process is further confirmed from the negative shift of the cathodic peak potentials on increasing the scan rate[9] (Fig. 4). The reduction peak current increased linearly with the square root of the scan rate over the range 50-500 mV s^{-1} (Fig. 5). The linearity indicates that the reaction rate is controlled by semi-infinite linear diffusion and can be also reflected in an uncomplicated redox reaction[10].

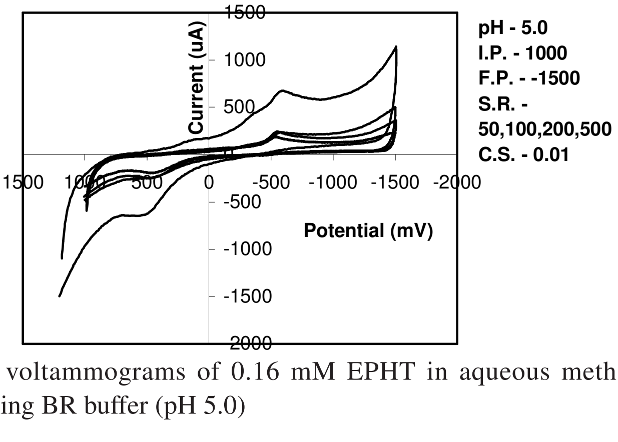


Fig. 1. Cyclic voltammograms of 0.16 mM EPHT in aqueous methanolic medium containing BR buffer (pH 5.0)

The electrochemical behaviour of EPHT was also studied at three different pH values 5.0, 7.0 and 9.0. The cathodic peak potentials shift towards negative values with an increase in pH indicates that the electrode reaction involves proton transfer and reduction becomes difficult at higher pH values[11]. The voltammetric data for reduction of EPHT to its products are given in Tables 1-3.

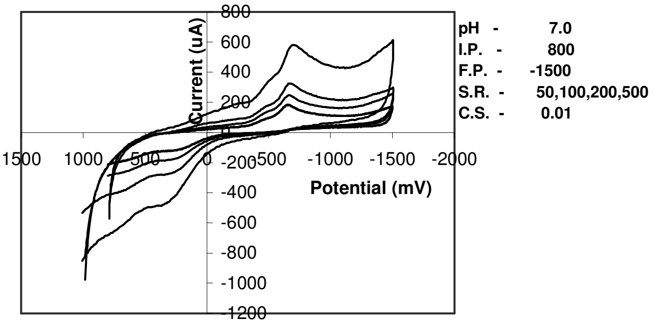


Fig. 2. Cyclic voltammograms of 0.16 mM EPHT in aqueous methanolic medium containing BR buffer (pH 7.0)

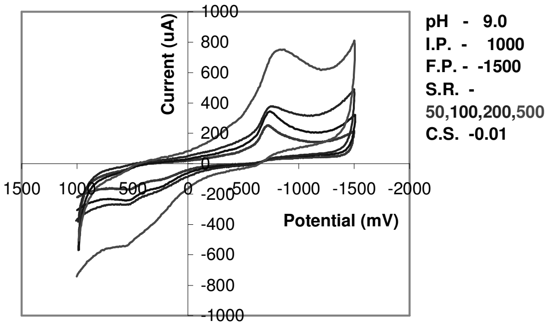


Fig. 3. Cyclic voltammograms of 0.16 mM EPHT in aqueous methanolic medium containing BR buffer (pH 9.0)

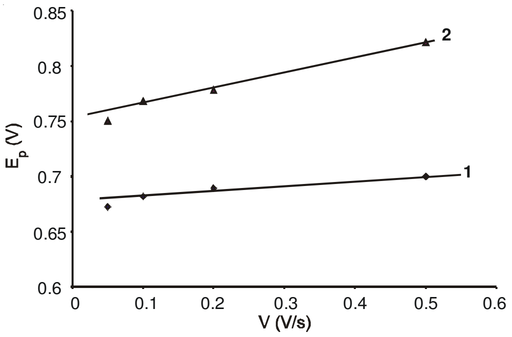


Fig. 4. Effect of scan rate (ν) on cathodic peak potential (E_p) at pH (1) 7.0 (2) 9.0

TABLE-1

EFFECT OF SWEEP RATE ON VOLTAMMETRIC PARAMETERS OF 0.16 mM EPHT IN AQUEOUS METHANOLIC SOLUTION CONTAINING BR BUFFER (pH 5.0)

S. No.	ν (mV/s)	E_p (mV)	$E_{p1/2}$ (mV)	I_p (mA)	$I_p/\nu^{1/2}$	αn
1	50	-561	-510	37	5.20	0.9350
2	100	-558	-508	59	5.90	0.9542
3	200	-582	-531	79	5.58	0.9350
4	500	-581	-525	123	5.36	0.8519

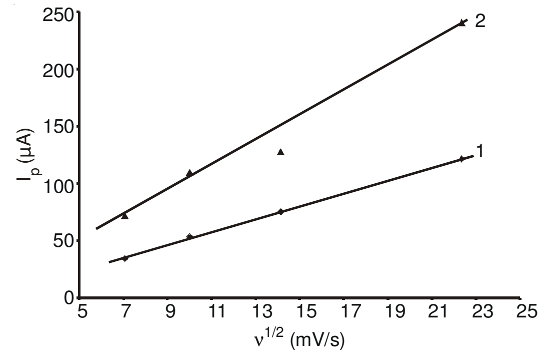


Fig. 5. Variation of cathodic peak current (I_p) *versus* $\nu^{1/2}$ at pH (1) 7.0 (2) 9.0

TABLE-2
EFFECT OF SWEEP RATE ON VOLTAMMETRIC PARAMETERS OF 0.16mM EPHT IN AQUEOUS METHANOLIC SOLUTION CONTAINING BR BUFFER (pH 7.0)

S. No.	ν (mV/s)	E_p (mV)	$E_{p1/2}$ (mV)	I_p (mA)	$I_p/\nu^{1/2}$	αn
1	50	-672	-615	34	4.80	0.8370
2	100	-682	-624	53	5.30	0.8225
3	200	-689	-638	75	5.30	0.9354
4	500	-700	-646	121	5.54	0.8835

TABLE-3
EFFECT OF SWEEP RATE ON VOLTAMMETRIC PARAMETERS OF 0.16 mM EPHT IN AQUEOUS METHANOLIC SOLUTION CONTAINING BR BUFFER (pH 9.0)

S. No.	ν (mV/s)	E_p (mV)	$E_{p1/2}$ (mV)	I_p (mA)	$I_p/\nu^{1/2}$	αn
1	50	-750	-667	71	10.04	0.5748
2	100	-768	-678	109	10.90	0.5301
3	200	-778	-676	127	8.98	0.4677
4	500	-821	-712	240	10.73	0.4377

To determine αn values the following expression was used[12-14];

$$E_{p1/2} = [E_p \pm 0.048/\alpha n]$$

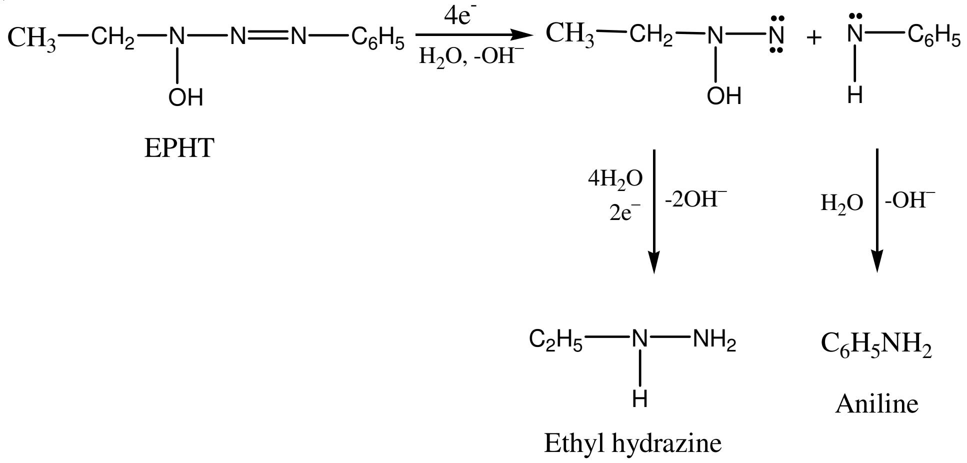
Here α is a reversibility criterion and n is number of electrons, which is same in all the cases under observation.

This electrochemical behaviour of EPHT is represented by the proposed reaction mechanism in acidic, aqueous and alkaline medium (**Scheme-I**). Since the steps involved in reaction mechanism occur at the same potential therefore only single reduction peak corresponding to transfer of six electrons[15] is observed in voltammograms.

The IR spectral results of products[16], ethyl hydrazine and aniline obtained after bulk electrolysis and separation are in confirmity with the proposed mechanism here.

Ethyl hydrazine exhibits absorption bands at 3230 cm^{-1} [ν(N-H)], 2960 cm^{-1} [ν(C-H) asymm], 2868 cm^{-1} [ν(C-H) symm], 1608 cm^{-1} [δ(N-H)], 1143 cm^{-1} [ν(C-N)] and aniline exhibits absorption bands at 3450 cm^{-1} [ν(N-H) asymm], 3350 cm^{-1}

[ν(N-H) symm], 3040 cm^{-1} [ν(Ar-H)], 1650 cm^{-1} [δ(N-H)], 1640-1450 cm^{-1} [ν(C=C) in plane skeletal vibrations], 1250 cm^{-1} [ν(C-N)], 750 cm^{-1}, 700 cm^{-1} [δ(C-H) mono substitution] in IR spectrum.



Scheme-I

The ^{1}H NMR spectrum of ethyl hydrazine reveals signals at δ 7.16 and δ 7.17, which indicates that two hydrogen of NH_2 are not magnetically equivalent, signal at δ 2.16 and δ 2.3 are assigned to ethyl protons and ^{1}H NMR spectrum of aniline reveals signals at δ 3.5 for NH_2 proton and δ 7.1 for aryl proton.

The cyclic voltammograms of EPHT were also recorded in potential range 1600-800 mV at different scan rates 100, 200, 300, 400, 500 mV/s in CH_2Cl_2 (Fig. 6). The repetitive scanning revealed the presence of cathodic peak at more negative potential indicating the irreversible reduction behaviour of electron transfer process.

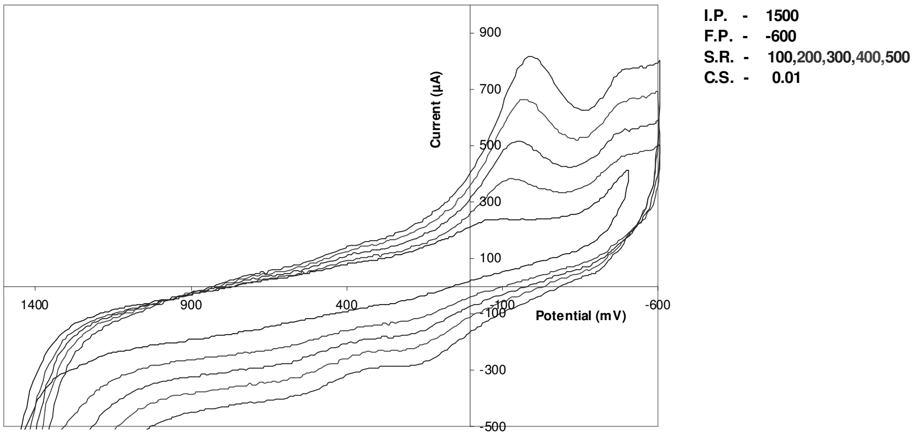


Fig. 6. Cyclic voltammograms of 1 mM EPHT in CH_2Cl_2

The shifting of cathodic peak potential of EPHT was found more negative in aqueous methanolic medium than that of in dichloromethane (CH_2Cl_2) which may be accounted due to low viscosity of CH_2Cl_2 and high solubility of ligand in CH_2Cl_2.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing necessary facilities and CSIR, New Delhi, for providing the financial assistance to one of us Manu Gupta.

REFERENCES

1. P.D. Chatlangya, C.S. Bhandari and N.C. Sogani, *J. Indian Chem. Soc.*, **54**, 1001 (1977).
2. R. Bhatt, A.K. Goswami, M.P. Tyagi and D.N. Purohit, *Asian J. Chem.*, **5**, 1143 (1993).
3. J. Eliassaf, J. Gaspariccaron, R.H. Sterzel, W. Czysz, M. Meyer zur Heyde, M. Bartuscaronek, F. Kreuzig, L. Johannsen and M. Katyal, *Fresenius' J. Anal. Chem.*, **289**, 289 (1978).
4. N. Naulakha and A.K. Goswami, *J. Indian Chem. Soc.*, **81**, 438 (2004).
5. V.S. Gurjar, P.S. Verma, S.K. Mukherji and K.N. Tondon, *Trans SAEST*, **28**, 145 (1993).
6. S.R. Yadav, P. Goyal, A. Sharma, P.S. Verma and I.K. Sharma, *J. Indian Chem. Soc.*, **79**, 695 (2002).
7. N.C. Sogani and S.C. Bhattacharya, *Anal. Chem.*, **28**, 81 (1956).
8. R. Karnawat, P.S. Verma and C.S. Bhandari, *J. Inst. Chemist. (India)*, **72**, 217 (2000).
9. P. Delahay, New Instrumental Methods in Electrochemistry, Ch. 6, Interscience, New York (1966).
10. A.J. Bard and R.L. Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, pp. 218-222 (1980).
11. P. Zuman and C.L. Perin, Organic Polarography, John Wiley and Sons, New York (1967).
12. J.A. Plambeck, Electroanalytical Chemistry: Basic Principles and Applications, John Wiley and Sons, New York (1982).
13. E.R. Brown and J.R. Sandifer, In Physical Methods of Chemistry, Electrochemical Methods, B.W. Rossiter and J.F. Hamilton, Vol. 2, John Wiley, New York (1986).
14. C.M.A. Brett and A.M.O. Brett, Electrochemistry: Principles, Methods and Applications, Oxford University Press, New York (1993).
15. L. Holleck and G. Kazemifard, *J. Electroanal. Chem.*, **35**, 369 (1972).
16. Allen J. Bard, Encyclopedia of Electrochemistry of the Elements (Marcel Dekker, Inc. New York), Vol. XIII (1973).

(*Received*: 26 February 2009; *Accepted*: 11 December 2009) AJC-8173