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Electrochemical Study of Cobalt (II) Complex with 3-Hydroxy-1,3-Diphenyltriazene

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ABSTRACT
Electrochemical Study of Cobalt (II) Complex with 3-Hydroxy-1,3-Diphenyltriazene(HT) have been studied in alcoholic-aqueous medium. This is first attempt to study HT – Co (II) complexes at d.m.e by Polarography technique in alcoholic- aqueous media in the B-R Buffer solution between the pH 7.5-8. The electrochemical reduction of the complex is diffusion controlled. Well defined waves are obtained and the $E_{1/2}$ shifts to more negative side with the addition of HPST. The reduction mechanism indicates two electron reversible reduction process and the stability constant Log β value found 7.5.
Keywords: Hydroxy triazene, polarography, electrochemical study, Co (II) - HT complexes study.

INTRODUCTION

Hydroxytriazenes are a class of chelating agents used extensively for Spectrophotometric studies of transition and non transition metals[1-3]. Although the ligands have been studied in details as spectrophotometric and complexometric reagents, hardly any attempt has been made on electrochemical behaviour of these ligands and their metal complexes. Even their electrochemical studies as ligands with transition metals are of recent origin[4]. Since the electrochemical behaviour of electron transfer processes are similar to biological processes.

In view of this the present studies HT- Co (II) complexes have been examined Polarographically at d.m.e in alcoholic-aquous media. The stability constants calculated values are in very good agreement with the results of Spectrophotometric studies of this system.

MATERIALS AND METHODS

Synthesis

3-Hydroxy-1,3-Diphenyltriazene (0.1M) has been synthesized by tree step method [11] in following manner. In this method nitrobenzene (12.3 ml) was reduced to Phenyl triazene in the presence of NH_4Cl (5.3 g) at 40-60°C with Zn dust (20g).

Second step involved the preparation of the diazotized product by adding 40 ml conc. HCl was added to sodium nitrite (6.9 g) solution in 500ml beaker with constant mechanical stirring. Beaker was placed in freezing mixture to maintain temperature between 0-5°C this mixture solution was added to thr aniline solution with constant mechanically stirring.

The third step coupling of phenyl hydroxylamine and diazoate products at 0-5°C in the pH range 4.5 - 6 with addition of sodium acetate buffer solution. After complete addition, The hydroxytriazene was obtained as yellowish[3] micro crystals after crystallization from double distilled water. Its purity was checked by the Physico Chemical Method like M.P and CHN analysis etc. Results of CHN and M.P. determined %C 67.5, %N 19.7, %H 4.8 and 119^{o}C respectively. Further the compound was subjected to IR spectral analysis which yielded the characteristics bands reported for hydroxytriazenes12 and their values for νO-H, νN-H, δN-H and δN-OH are 3415, 3180, 1515 and 1068 respectively. The result establishing purity of compound.

Apparatus and solutions

A Systronics Polarograph 1632 was used for obtaining current- voltage curves. Metal solution (1M) was prepared using Cobalt Acetate hexa hydrated and ligand solution was prepared by dissolving HT (0.01M) in alcohol-distilled water solution (60:40). Briton-Robinson buffer was used to maintain pH of electrolyte solution. Ionic strength was kept constant by using KCl as supporting electrolyte. Gelatin (0.002%) was used as maximum suppressor. The d.m.e. having the following characteristics m = 1.35 mg/sec. t = 1 sec per drop. Solution was deaerated by purging of oxygen free nitrogen through the polarographic cell. Temperature was maintained at 298 K.

The electrochemical behavior of Co (II) – HT has been studied at d.m.e. in aqueous medium. The shift of half-wave potentials towards a more negative value[4] with increasing concentration of ligand indicated complex formation and the diffusion current was found to decrease regularly with increase of HT concentration.

Table-1: Polarographic Characteristics of CO(II) - 3-Hydroxy-1,3- Di Phenyltriazene

S.No.	C_x (mol/lit)	Log C_x	$E_{1/2}$ (-V v/s SCE)	I_{max} (µA)	i (µA)	i_d (µA)	Log $[i/(i_d-i)]$	Log β
1	0.02	-1.6989	1.231	51	43.71	44	2.178	8.1
2	0.04	-1.3979	1.265	37	31.71	32	2.0387	7.74
3	0.06	-1.2218	1.285	36	30.85	31.5	1.6763	7.53
4	0.08	-1.0969	1.3	30	25.71	37	0.3574	7.94
5	0.1	-1	1.31	28	24	36	0.301	7.2
6	0.12	-0.9208	1.32	27	23.14	35	0.2902	7.19
7	0.14	-0.8538	1.33	24	20.57	34	0.1851	7.17
8	0.16	-0.7958	1.339	22	18.85	33	0.1245	7.17

Log β = 7.5

RESULTS AND DISCUSSION

Diffusion controlled nature of each wave was verified by id Vs C and id Vs $\sqrt{h}$ plots. The plots were linear in both the cases indicating diffusion controlled nature of the process.

Investigation of the nature of reduction process and determination of n (By Heyrovsky-Ilkovic Equation): The slope value of linear plots of $\log\left(\frac{i}{id-i}\right)$ Vs E_{de} found to be in the range of 30-32 mV, thereby showing the reversible nature of reduction process involving two electrons.

The plots of $E_{1/2}$ Vs log Cx have been found to be a straight line showing the formation of most stable complex. The value of coordination number J as determined by slope is 4. This shows that the complex composition is in 1:2 (M: L) ratio.

The stability constant of the Co (II) – HT complex has been determined by classical method of Lingane [6], as this method is applicable for maximum coordination number and for the stability constant of highest complex formed. The $E_{½}$ has a linear correlation with ligand concentrations; which shows that there is only one complex formed in the solution. The following equation has been used to calculate the stability constant of the complex studied.

$$\Delta E_{\frac{1}{2}} = \frac{.0591}{n}\log\beta + j\frac{.0591}{n}\log C_x$$

Here,

$\Delta E_{1/2}$ = Difference of half wave potentials of simple metal ion and complexed ion.

n = Number of transferred electrons

Log β = Stability constant of complex formed.

j = Coordination number

C_x = Concentration of ligand

Thus, the value of log β has been found to be 7.5

CONCLUSION

The present work has opened up possibility of studing Co(II) – hydroxytriazenes complexes by electrochemical method particularly sampled D.C. polarography. Results obtained with polarography and the log β values obtained are in quite good agreement with those obtained with spectrophotometric studies of similar compounds. This proves the validity of polarographic technique for studies of hydroxytriazene metal complexes[5].

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