

Synthesis, characterization and spectrophotometric studies of hydroxytriazene - palladium complexes

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Abstract- A simple and sensitive spectrophotometric method is proposed for the determination of Palladium (II) in ppm level using sulphaguanidine based hydroxytriazenes as spectrophotometric reagent. The proposed reagent form pale yellow and light brown coloured complexes with Pd (II) in alcoholic medium at pH range 1.8-2.8. The mean values of molar absorptivity and Sandell's sensitivity were calculated and were found to be 15477, 3179 Lmol⁻¹cm⁻¹ and 6.87, 12.55 mg.cm⁻¹ respectively for complex I, II. The composition of Pd (II) - reagent complexes were found to be (Metal- Ligand) ML₂. The interference of different cations and anions were also studied. Thus a new method for Pd (II) determination has been developed. The method can be applied to biological samples also for detection of Pd (II).

Index Terms- Hydroxytriazene; Spectrophotometric Studies; Sulphaguanidine; Pd metal; Hydroxytriazene- Pd complexes.

1. INTRODUCTION

Palladium was discovered in 1803 by William Hyde Wollaston. It is a platinum group element and mostly used in catalytic convertor, jewelry trades [1] and dentistry [1]. It is also used for hydrogen gas purification, storage [2], watch making, in making surgical instruments and electrical contacts. In recent years it has been reported that palladium containing dental implants can cause allergic contact dermatitis [3]. Thus for the determination of palladium a simple, selective and sensitive method is explored.

Hydroxytriazene possess the functional group [-N(OH)-N=N-]. Importance of this class of compounds as chelating agents [4-6] and complexing ability [7-9] is now well established. The analytical utility and studies on metal complexes have been explored exhaustively in our laboratory. Lately a number of hydroxytriazenes have been selected for anti-inflammatory [10], antibacterial [11-12], antifungal [12], insecticidal [13], wound healing [14], analgesic agents [15], photo labile [16] reagents and electrochemical studies [17]. Sulfa drugs are well known antibiotics. However, a very few sulpha drug based hydroxytriazenes are used for spectrophotometric determination [18-22] of metals. In the present paper two new reagents derived from sulphaguanidine have been used for the spectrophotometric studies of Pd (II). The reagents have been synthesized using standard methods [23-25] and the purity of the product were checked by spot test, M.P., IR, NMR, and MASS spectral analysis. On the basis of spectrophotometric studies the composition of complexes of Pd (II) is found to be 1:2.

2. EXPERIMENTAL

Reagents were synthesized as per standard method using AR grade chemicals. The synthesis is completed in three steps.

2.1 Step-1: Preparation of hydroxylamine

In the preparation of hydroxylamine, 0.1 mole of nitro compound, 0.1 mole of NH₄Cl and 75 (50 ml water+25 ml spirit) ml solvent were mixed and stirred mechanically at 40°C and then 20 gm of Zn dust was added in the small lots to maintain temperature of the reaction between 40-60°C. After one hour the reaction mixture was filtered and the solution obtained was kept in refrigerator at about 0°C which was further used for coupling.

2.2 Step-2: Preparation of diazonium salts

4-Amino-N-(aminoiminomethyl)benzenesulfonamide (0.05 mole) was dissolved in mixture containing 25 mL of HCl and 25 mL of water. In other beaker 0.05 moles sodium nitrite was dissolved in required quantity of water. The temperature of the reaction mixture was maintained between 0-5°C. To this solution, sodium nitrite (NaNO₂) solution was added drop by drop with continuous stirring. The diazotized product so obtained was directly used for coupling.

2.3 Step-3: Coupling

The temperature of both products obtained from step-1 and step-2 were maintain between 0-5°C. Then Step-2 solution was added to solution obtained in step-1 with continuous stirring and pH of the solution was maintained between 5-6 by adding sodium acetate

solution. The resultant product of coupling was filtered under suction, washed with ice-cold water and then dried. The crude compounds were purified and recrystallized. The purity of hydroxytriazenes were checked by I.R, ¹H NMR and melting point

determination. Their compositions were verified by elemental analysis.

The synthetic scheme can be represented as

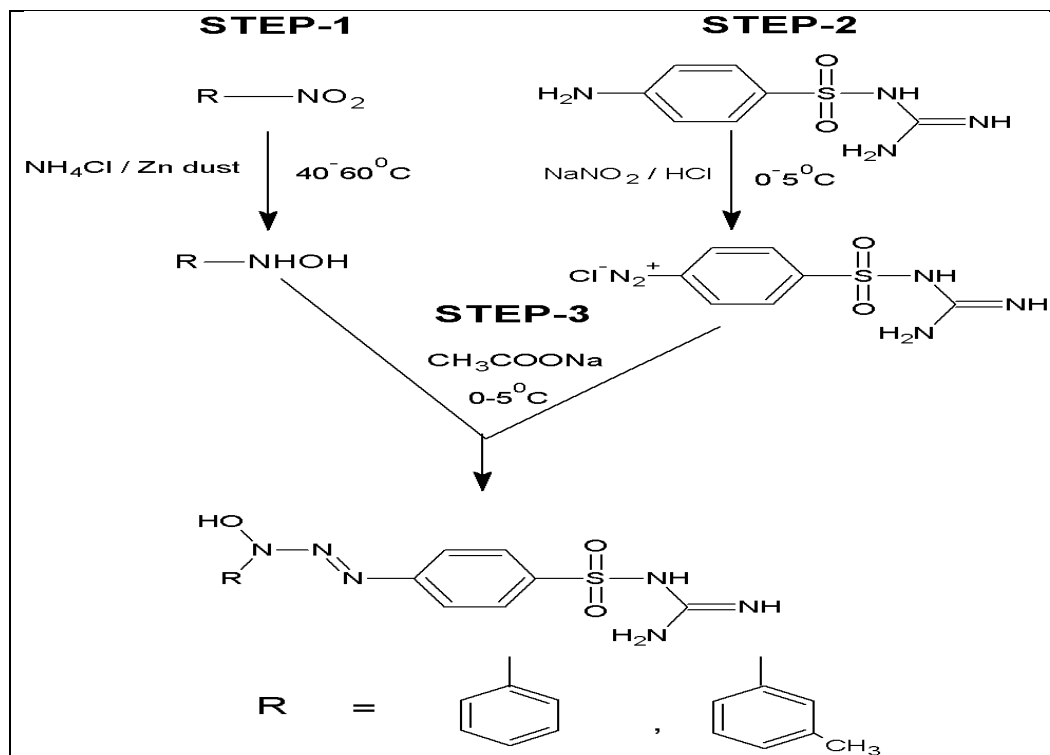


Table 1. Physical Characteristics of the reagents

Reagent	Molecular Formula	Colour and Shape of the reagent	M.P. °C	Analysis		Structure
				Calculated	Experimental	
3-hydroxy-3-phenyl-1-(4-carbamimidoylsulfonyl)phenyltriazene	C ₁₃ H ₁₄ N ₆ O ₃ S	Light yellow crystal	166	C- 46.70% H- 4.22% N- 25.14%	C- 45.96% H- 4.02% N- 24.91%	
3-hydroxy-3-(3-methylphenyl)-1-(4-carbamimidoylsulfonyl)phenyltriazene	C ₁₄ H ₁₆ N ₆ O ₃ S	Off white powder	162	C- 48.27% H- 4.63% N- 24.12%	C- 47.96% H- 4.32% N- 23.82%	

3. Characterization data of synthesized hydroxytriazenes

3-hydroxy-3-phenyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene : IR 3439(_O-

H), 3344(_{N-H}), 1619(_{C=N}), 1524(_{N=N}), 1134(_{S=O})cm⁻¹; ¹H NMR (DMSO): δ: 12.36(1H,s,OH), 7.5-8.2(9H,m,ArH), 6.62(1H,s,SO₂NH), 3.33(4H,s,NH₂), Mass; (m/z) M+ 335.37.

3-hydroxy-3-(3-methylphenyl)-1-(4-carbamimidoylsulfamoyl)phenyltriazene : IR 3436(O-H), 3344(N-H), 1618(C=N), 1522(N=N), 1134(S=O)cm⁻¹; ¹HNMR (DMSO): δ: 12.18(1H,s,OH), 7.3-

7.8(9H,m,ArH), 6.65(1H,s,SO₂NH), 3.30(4H,s,NH₂), Mass; (m/z) M+ 349.47.

4. SPECTROPHOTOMETRIC STUDIES OF Pd (II) COMPLEXES

reagent blank. The optimum pH range for constant maximum absorbance was selected.

4.1 Standard solution of Pd (II)

A fresh stock solution of 10⁻² M was prepared by dissolving the requisite quantity of palladium chloride (PdCl₂) in the minimum volume of hot concentrate HCl and diluting with double distilled water. The solution was then standardized complexometrically with EDTA, ammonium acetate and standard ferric ammonium sulphate solutions using sulfosalicylic acid as an indicator. Dilute solution is prepared using stock solution when required.

4.7 Composition of the Pd (II) complex

The composition of the Pd (II) complex was determined using Job's method and mole ratio method of Yoe and Jones. The composition as determined by both the method agreed well.

4.2 Reagent solution

A stock solution of 10⁻³ M is prepared by dissolving the required amount of corresponding hydroxytriazene in alcohol. Solutions of desired concentrations were prepared by appropriate dilution of the stock solution with alcohol when required.

4.8 Job's method

In this method set of solution was prepared by varying the volume of equimolar Pd (II) and reagent solution from 0 to 3 ml. After pH adjustment the solution were made up with alcohol. The absorbance of solution was measured at working wavelength against reagent blank. The composition of complex was found to be 1:2 [Pd: R]. Various reagents and their complex composition with Pd (II) have been tabulated in Table-2

4.3 Solutions for pH adjustment

4.3.1. Tris buffer solution

A 1% tris (hydroxymethyl) amino methane solution was prepared by dissolving 1.0 gm of the tris buffer in minimum quantity of distilled water with making it up to 100 ml.

4.9 Mole ratio method:

Mole ratio method of Yoe and Jones has been applied to determine stoichiometry of the complexes. In which the concentration of Pd (II) was kept constant and reagent concentration was varied. A series of solution having Pd (II):R ratio 1:1 to 1:10 were prepared with maintaining the pH of constant absorbance. Absorbance of each solution of a set was measured at working wavelength against reagent blank. The composition was found to be 1:2 [Pd:R] by this method. It agree with the ratio determination by Job's method, thus proving Pd (II)-hydroxytriazenes for 1:2 Pd (II):R complexes. The complex composition have been tabulated in Table-2.

4.3.2. Perchloric acid solution

A 1 % solution of Perchloric acid was prepared by dissolving 1.0 ml of the Perchloric acid in minimum quantity of distilled water with making up to 100 ml.

4.4 Instrument

ELICO double beam SL 210 UV-VIS spectrophotometer was used for study.

4.10 Beer's validity law

A set of solution having M:L ratio 1:10 was prepared. The studies were completed under optimum condition of pH, concentration and solvent at corresponding working wavelength. The absorbance was consider for the complex against the reagent blank.

4.5 Selection of suitable working wavelength

To selected a suitable working wavelength, Solution of Pd : R in 1:10 ratio were prepared in 10 ml volumetric flask with alcohol. Absorbance of solution against its reagent blank was measured in the wavelength region 300-600nm. The suitable working wavelength is chosen in a region where the absorption of Pd (II) complex was maximum and absorption due to reagent was minimum.

4.11 Sandell's sensitivity:

The molar absorptivity of the Pd (II) complexes was measured from the Beer's law graph and the value thus obtained was used to determine Sandell's sensitivity of the complex. The values show that the method used is quite sensitive and satisfactory for the determination of Pd (II).

4.6 Effect of pH on absorbance

Absorbance of each solution at various pH values containing Pd (II) and reagent solution in 1:10 ratio was carried out at suitable working wavelength against

Table 2. Spectrophotometric Determination of Pd (II) with Reagents

S. No.	Pd (II) complex with reagent	Job's / Mole ratio Composition of the complex [Pd(II) : R]	Working wavelength or λ max (nm)	Optimum pH range	Molar absorbtivity [$L.mol^{-1}.cm^{-1}$]	Sandell's sensitivity [$mg.cm^{-2}$]
1	3-hydroxy-3-phenyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene	1 : 2	408	1.8 – 2.2	15477	6.87
2	3-hydroxy-3-(3-methylphenyl)-1-(4-carbamimidoylsulfamoyl)phenyltriazene	1 : 2	416	2.2 – 2.8	8477	12.55

5. RESULT AND DISCUSSION

As described above hydroxytriazenes form 1:2 complexes with Pd (II), Hydroxytriazenes act as bidentate ligand which indicates a tetra-coordinated Pd (II) complex with probable square planer geometry. Thus, a series of reagents prepared from sulfa drug moiety have been used for determination of Pd (II) would also add to the understanding of Pd (II)-HT complexes.

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