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Spectrophotometric studies of 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl)phenyltriazeno-Iron (III) complex

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Abstract: A number of hydroxytriazenes have been used as analytical reagents for various transition metals. In the present paper spectrophotometric studies of 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl) phenyltriazeno in the determination of Fe(III) is being reported. The complex absorbs at 403 nm and form 1:2 complex with Fe(III) in the pH range of 1.4-2.0.

Keywords: 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl)phenyltriazeno, spectrophotometric determination, Fe (III).

Introduction:

The complexing ability of hydroxytriazeno has been explored exhaustively in our laboratory during last many years¹⁻⁷. However, very few hydroxytriazenes based on sulfa drugs have been used as analytical reagents for spectrophotometric determination of transition metal although they can be biologically active compounds. In view of this, in the present investigation a new reagent 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl) phenyltriazeno derived from sulfacetamide has been chosen for spectrophotometric studies of Fe(III) complex. The reagent 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl) phenyltriazeno has been synthesized using standard methods⁸⁻¹⁰ and product formed was

first checked for purity by spot test and then subjected to IR, ¹HNMR, ¹³CNMR, MASS spectral analysis for verifying the purity of compounds.

Material and Methods:

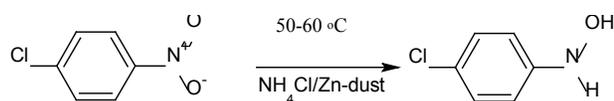
All chemicals used in experiment were commercially purchased and used without further purification.

Chemistry

3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl)phenyltriazeno was synthesized as per standard method. The general method is described in reaction scheme 1. The synthesis has been done in three steps.

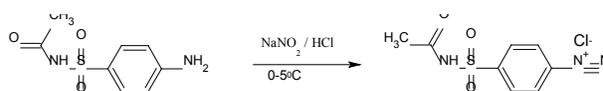
Step 1: Reduction of p-chloronitrobenzene

In a 250 mL beaker (0.03 mol) of p-chloronitrobenzene, 1.0647 gm of NH_4Cl , 21 mL water and 21 mL $\text{C}_2\text{H}_5\text{OH}$ mixed. Mixture being stirred mechanically, 6 gm Zn dust added in small lots such that the temperature of reaction mixture remained between 60 to 65°C. Addition of Zn dust completed in 40 min. The reaction mixture stirred mechanically for another 15 min. The solution filter under suction and washed with ice cold water. The filter was taken in a beaker kept in freezer and used as such for coupling with diazotized product.

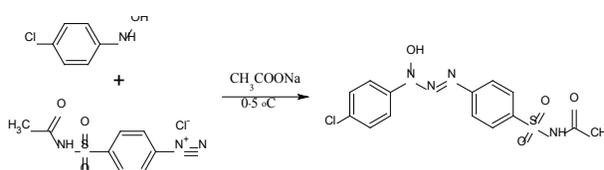
**Step 2: Diazotization of N-[(4-aminophenyl)sulfonyl]acetamide**

In a 250 mL beaker 0.02 mol of N-[(4-aminophenyl)sulfonyl]acetamide dissolved in warm mixture of 5 mL concentrated HCl and 5 mL of water. After constant stirring the mixture kept in a ice bath to cool. In another beaker 1.38 gm. of NaNO_2 dissolved in appropriate amount of water and kept in the same ice bath. After maintenance of temperature the beaker which contained N-[(4-aminophenyl)sulfonyl]acetamide solution NaNO_2 solution is added

drop by drop with continuous stirring. The diazotized product so obtained, used directly for coupling.

**Step 3: Coupling**

The p-chlorophenylhydroxylamine prepared in step first was coupled with the diazotized product of second step at 0°C to 5°C under mechanical stirring with ice bath by addition of sodium acetate solution for maintaining the pH close to 5 during coupling process. The compound 3-hydroxy-3-(4-chlorophenyl)-1-(4-(4-acetylsulfamoyl)phenyl)triazene obtained as brownish yellow precipitate, which recrystallized several times in ethanol. The final product obtained in the form of light yellow crystal.



3-hydroxy-3-(4-chlorophenyl)-1-(4-(4-acetylsulfamoyl)phenyl)triazene

Table 1. Physical Characteristics, M.P., C H N Values of the reagent

Molecular Formula	Melting Point (°C)	Colour and shape of the crystal	% Analysis					
			Calculated			Experimental		
			C %	H %	N %	C %	H %	N %
$\text{C}_{14}\text{H}_{13}\text{ClN}_4\text{O}_4\text{S}$	215°C	Light Yellow Needle	45.59%	3.55%	15.19%	44.95%	3.40%	14.98%

Characterization data of 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfamoyl)phenyl triazene: (C₂H₅OH) IR: 3340, 3260, 2918, 1718, 1578, 1298, 1135 cm⁻¹; ¹H NMR (DMSO): δ 12.454 (1H, s), δ 8.11-7.84 (2H, d), δ 7.666-7.643 (2H, d), δ 7.621-7.59 (2H, d); δ 7.421-7.393 (2H, d), δ 2.490 (1H, s), δ 1.907 (1H, s); ¹³C NMR (300 MHz, DMSO) δ 168.7126, 144.5996, 141.6344, 134.8172, 132.1379, 129.4492, 129.3157, 121.8215, 114.7373, 23.2245 ppm; ESI-HRMS for C₁₄H₁₃ClN₄O₄S, calcd. 368.7954, found 370.4

Determination of complex composition of Iron (III): 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfamoyl)phenyl triazene complex

Procedure: Following set of experiments were carried out for the spectrophotometric determination of Fe(III).

(i) **Reagent solution:** A fresh stock solution of the reagent 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl) phenyl triazene (1.0 × 10⁻² M) was prepared by dissolving appropriate quantity of the reagent in absolute alcohol. Dilute solution were prepared from this stock solution as and when required.

(ii) **Standard solution of iron(III):**

A 100 mL amount of stock solution (1.0 × 10⁻² M) of trivalent iron was prepared by dissolving 290 mg of ferric Nitrate (A.R.) in doubly distilled deionized water containing 1-2 mL of nitric acid (1+1). The standardization of above prepared solution has been made by using 1.0 × 10⁻² M EDTA Solution at constant pH using sulphosalicylic acid as indicator. More dilute standard solutions were prepared from this stock solution as and when required.

(iii) **Solution for pH adjustment:**

a) Tris buffer solution: 1% tris buffer solution was prepared by dissolving 1 gm of tris buffer in

double distilled water.

Method:

Determination working wavelength

The spectrum of the complex formed with each reagent ([M]:[R]) was obtained in wavelength region 300 nm to 700 nm against reagent blank. Further, spectrum of reagent was also measured in the same wavelength region against acetone. The working wavelength was chosen such that there was maximum difference between the absorbance of the complex and the reagent.

Effect of pH on absorbance:

The absorbance of a series of solutions containing Fe(III) and reagent in the molar ratio 1:10 ([M]:[R]) was measured against reagent blank at corresponding working wavelength at various pH values to determine pH range of constant and maximum absorbance varying from 1.0-5.0. The color that developed in pH range of constant absorbance was bluish black for each reagent. The color development in each case was instantaneous and stable for about 24 hours. All the measurements were made at room temperature in all the three cases.

Conformity with Beer-Lambert's Law

Under optimum conditions of pH, solvent and Iron (III) to reagent ratio, the validity of Beer-Lambert's law was studied. The results of absorbance obtained were plotted against the corresponding concentration of iron (III). The calibration curve obtained was used to determine the concentration of iron in sample and digestion blank. The difference between these absorbance was taken as the absorbance corresponding to the sample.

Determination of Molar Composition of Iron (III) Complex

Two different methods, namely; Job's method and Mole ratio method were used for the determination of molar composition of metal:

reagent.

(a) Job's method:

The composition of Fe(III) complex was determined by varying volume of equimolar solution concentration of both reagent and Fe(III) in the sample. After pH adjustment, the solutions were made up to 10ml with ethanol. The absorbance of solution was measured at suitable working wavelength against reagent blank. The second set of this method differed from the first set only in the concentration used. By this method the composition was found to be 1:2 [Fe:R].

(b) Mole ratio method of Yoe and Jone's:

In this method Fe(III) concentration was kept constant and reagent concentration was varied. A series of solutions having Fe(III) to reagent ratio 3:1 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 the reagent blank. By this method the composition was found 1:2 [Fe:R].

Sandell's sensitivity:

The molar absorptivity of the Fe(III) complex was calculated from the Beer's law graph and it was found to be $\epsilon = 0.991 \times 10^4 \text{ L/mol.cm}$. The value thus obtained was used for determining Sandell's sensitivity of the complex obtained is $5635.21 \text{ mg.cm}^{-2}$. This value shows that the method used is quite sensitive and satisfactory for the determination of Fe(III).

The above studies determine composition of Fe(III)-Hydroxytriazene complex to be 1:2 and Sandell's sensitivity values indicates that the reagents fairly sensitive for Fe(III). Conclusively a drug based reagent has been developed which can be used for determination of Fe(III).

Table. 2: Spectrophotometric determination of Fe(III) with

Fe(III) complex with reagent	Composition of the complex [Fe(III) : R]	Working Wavelength or λ_{max} (nm)	Optimum pH range	Beer's Law range (M)	Molar absorptivity [$\text{L.mol}^{-1}.\text{cm}^{-1}$]	Sandell's Sensitivity mg.cm^{-2}
3-hydroxy-3-(4-chlorophenyl)-1-(4-acetyl sulfamoyl) phenyltriazene	1:2	403 nm	1.4-2.2	1.0×10^{-6} to 3.0×10^{-5}	0.991×10^4	5635.21

References

1. K. Paliwal, D. Gorji, S. Kumar, N. Naulakha, A.K. Goswami, D.N. Purohit, Asian J. Chem. **2001**,13, 299-304.
2. K. Sharma, U. Maroo, R.S. Chauhan, A.K. Goswami, D.N. Purohit, Oriental J. chemistry **1999**, 15, 177-78.
3. Tushita Babel, Amit Bhandari, Preksha Jain, Anita Mehta, A. K.Goswami, Int Res J Pharm **2012**, 3(5), 382-385.
4. Neelam Naulakha, A. K. Goswami, J Indian Chem. Soc. **2004**, 81(5), 438-439.
5. Saba Khan, Rekha Dashora, Anita Mehta, A. K. Goswami, J Indian Chem Soc **2003**, 80(8), 793-794.
6. Rekha Bhatt, B. Rezaie, A. K. Goswami, R. S. Chauhan, D. N. Purohit, J Indian Chem Soc **1996**, 73(1), 89.
7. Rajendra S. Shekhawat, Rakesh S. Shekhawat, R. Singh, R. S. Chauhan, A. K. Goswami, D. N. Purohit, Asian J. Chem., **13(2)**, 783,(2001).
8. Elkins M., Hunter L., J Chem Soc (London) **1938**, 1346.
9. Sogani N.C., Bhattacharya S.C., Anal Chem **1956**, 28, 81.
10. Sogani N.C., Bhattacharya S.C., J Indian Chem Soc **1959**, 36, 363.