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

Shilpa Agrawal, Shilpa Jain and A K Goswami*

Coordination laboratory, Department of Chemistry, MohanlalSukhadia University, Udaipur- 313001, Rajasthan Email: akumargoswami@rediffmail.com
Received 4 December 2015; Accepted 31 December 2015

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)phenyltriazene 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)phenyltriazene, spectrophotometric determination, Fe (III).

Introduction:
The complexing ability of hydroxytriazenes 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)phenyltriazene derived from sulfacetamide has been chosen for spectrophotometric studies of Fe(III) complex. The reagent 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfonyl)phenyltriazene has been synthesized using standard methods8-10 and product formed was first checked for purity by spot test and then subjected to IR, 1H NMR, 13C NMR, 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)phenyltriazene 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 NH4Cl, 21 mL water and 21 mL C2H5OH 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 an ice bath to cool. In another beaker 1.38 gm. of NaNO2 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 NaNO2 solution is added drop by drop with continuous stirring. The diazotized product so obtained, used directly for coupling.

3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfamoyl)phenyltriazene obtained as brownish yellow precipitate, which recrystallized several times in ethanol. The final product obtained in the form of light yellow crystal.

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

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Melting Point (°C)</th>
<th>Colour and shape of the crystal</th>
<th>% Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C %</td>
</tr>
<tr>
<td>C14H13ClN4O4S</td>
<td>215°C</td>
<td>Light Yellow Needle</td>
<td>45.59%</td>
</tr>
</tbody>
</table>

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-acetylsulfamoyl)phenyltriazene 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-acetylsulfamoyl) phenyltriazene
Characterization data of 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfamoyl)phenyl triazene: (C$_7$H$_5$OH) IR: 3340, 3260, 2918, 1718, 1578, 1298, 1135 cm$^{-1}$; $^1$H NMR (DMSO): $\delta$12.454 (1H, s), $\delta$8.11-7.84 (2H, d), $\delta$ 7.666-7.643 (2H, d), $\delta$7.621-7.59 (2H, d); $\delta$7.421-7.393 (2H, d), $\delta$2.490 (1H, s), $\delta$1.907 (1H, s); $^{13}$C NMR (300 MHz, DMSO) $\delta$ 168.7126, 144.5996, 141.6344, 134.8172, 132.1379, 129.4492, 129.3157, 121.8215, 114.7373, 23.2245 ppm; ESI-HRMS for C$_{14}$H$_{13}$ClN$_4$O$_4$S, calcd. 368.7954, found 370.4

Determination of complex composition of Iron (III): 3-hydroxy-3-(4-chlorophenyl)-1-(4-acetylsulfamoyl)phenyltriazene 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) phenyltriazene (1.0 $\times$ 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 $\times$ 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 $\times$ 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 1gm 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 regent 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 $\varepsilon = 0.991 \times 10^4 \text{L/mol.cm}$. The value thus obtained was used for determining Sandell’s sensitivity of the complex obtained is 5635.21mg.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

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

References