

Synthesis and characterization of bromo substituted o-hydroxy oximes and thiosemicarbazone ligands used as chelating reagents

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(Received: April 12, 2008; Accepted: June 04, 2008)

ABSTRACT

A new class of bromo substituted o-hydroxy oximes and thiosemicarbazones have been prepared by using Resorcinol and characterized on the basis of elemental, IR and UV spectral studies. The ligands 2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO) and 4-phenyl-3-thiosemicarbazone of 2-hydroxy-4-n-propoxy-5-bromoacetophenone (HnPBAPT) formed, act as an organic chelating reagent for the rapid determination of transition metal ions spectrophotometrically. Both ligands obtained were selective and sensitive.

Key words: Ligand, Oximes, IR Spectra, UV spectra, Thiosemicarbazone.

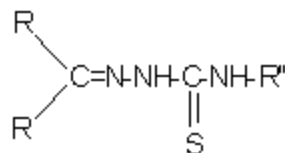
INTRODUCTION

Organic reagents have been employed in various ways for the detection and determination of transition metal ions. At present they are rapidly gaining in popularity owing to their greater sensitivity and specificity as compared to inorganic reagents, and also because of the greater convenience with which they may be employed in many analytical procedures¹⁻³. Among the salt forming groups, the important ones are -OH, -COOH, -SH, =NH etc. Out of these hydrogen of -OH in alcohols is not sufficiently acidic and thus favours salt formation. But when it is joined to benzene ring, it becomes sufficiently acidic. The value of such group is immeasurably enhanced, if in addition to the acidic group, the molecules possess a group which forms a cyclic structure giving chelate compounds.

Resorcinol (m-Dihydroxybenzene), the starting material for the preparation of the ligands

HnPBAO and HnPBAPT is prepared by alkaline fusion of benzene-disulphonic acid. It is a colourless crystalline solid (m.p 110°C) very soluble in water, alcohol and ether. It is used for making dyes and in pharmaceutical industries.

Both oximes and thiosemicarbazones have also been widely used as analytical reagents. The general structure of thiosemicarbazones is as under:



Where R, R' = H, Alkyl or aryl group.

R'' = H, Alkyl or aryl group.

Thiosemicarbazones act as good chelating agents forming chelates with various ions by bonding through thioketo sulphur atom and hydrazine nitrogen atom. Thiosemicarbazones obtained behave as unidentate or bidentate or multidentate ligand depending upon the aldehyde or ketone used for condensation. They are oxidized easily and this property is utilized for the determination of oxidants. K.H.Reddy and D.V. Reddy⁴ used cyclohexane-1,3-diene-bisthiosemicarbazone monohydrochloride as an organic reagent for the determination of transition metal ions.

Oximes of resacetophenone and its substituted derivatives have been studied as chelating agents for the estimation of bivalent metals [5,6]. An attempt was made to improve upon the efficiency of resacetophenone oxime as chelating reagent by making it more sensitive in the following ways

A chromophore was added to the molecule to make it coloured so that completion of the precipitation of the bivalent metal could be more easily observed.

Increasing the molecular weight of the oxime, results in an increase in the weight of the chelate and in this way the experimental error could be minimized.

From the review of literature, it was found that bromo substituted o-Hydroxy ketoximes are less used as analytical reagents for different transition metal ions. Hence, by keeping the above points in mind, we synthesized 2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO) and 4-phenyl-3-thiosemicarbazone of 2-hydroxy-4-n-propoxy-5-bromoacetophenone (HnPBAPT).

EXPERIMENTAL

All the chemicals and salts used for the present study were obtained from s.d.fine chemicals (India), with purity greater than 99% and of analytical grade. The absorbance measurements were done on a "Milton Roy" (Spectronic 20D+) spectrophotometer and Shimadzu UV-160A (UV-Visible spectrophotometer). All the pH measurements were done on Equip-tronic electronic

pH-meter (Model EQ-614) and required pH was maintained using sodium acetate-acetic acid and sodium acetate-HCl buffers of suitable concentration. The IR spectra was recorded on Shimadzu -Japan spectrophotometer (Model:FTIR-801) using KBr pellets. The weighing was done on a "AE-163" single pan electronic balance with a precision of ± 0.1 mg.

Synthesis of 2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO):-

Resacetophenone [I] was prepared according to method of Robinson and Shah[8], using resorcinol, acetic acid and anhydrous zinc chloride. Resacetophenone (7.45 gm, 0.05mole) was dissolved in minimum amount of glacial acetic acid. Bromine in acetic acid (8gm, 0.05 mole) was added dropwise, with continuous stirring, to the reaction mixture. After complete addition of bromine solution, it was allowed to stand for one and a half hour in a water bath. The contents were poured on ice-cold water. The product obtained was separated and washed with saturated solution of sodium bisulphite to remove excess bromine and then with water to get colourless 2,4-dihydroxy-5-bromoacetophenone [II] crystals.

A mixture of 2,4-dihydroxy-5-bromoacetophenone [II] (23.1gm), n-propyl iodide (17gm) and anhydrous potassium carbonate (13.8gm) in acetone (150ml) was refluxed on water bath at 65-70°C for 6-8 hours. Excess acetone and n-propyl iodide was distilled off and residue left was treated with diluted hydrochloric acid till there was no effervescence of CO₂. The contents were poured over ice. The solid separated was crystallized from ethanol (m.p 134 \pm 1°C). The product obtained was 2-Hydroxy-4-n-propoxy-5-bromoacetophenone [III]. 2-Hydroxy-4-n-propoxy-5-bromoacetophenone (3gm) was dissolved in minimum quantity of ethanol. Aqueous solution of hydroxylamine hydrochloride (6gm) and sodium acetate (10gm) was added to it. A little more alcohol was added to get clear solution. The solution was refluxed on a water bath at 75-80°C for 4 hours. The mixture was poured on crushed ice and a light green solid separated. It was crystallized from ethanol (m.p 172 \pm 1°C). The product obtained was 2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime [IV] (HnPBAO).

Table 1: Physical and analytical data of ligands

Ligand	Colour	m.p. (°C)	Analysis % found (Calcd)		
			C	H	N
HnPBAO(C ₁₁ H ₁₄ O ₃ NBr)	Light green	172	46.12(45.83)	4.72(4.86)	4.68(4.86)
HnPBAPT(C ₁₈ H ₂₀ O ₂ N ₃ SBr)	Yellowish Orange	160	51.48(51.18)	4.64(4.73)	9.73(9.95)

Table 2: IR spectra of HnPBAO and HnPBAPT

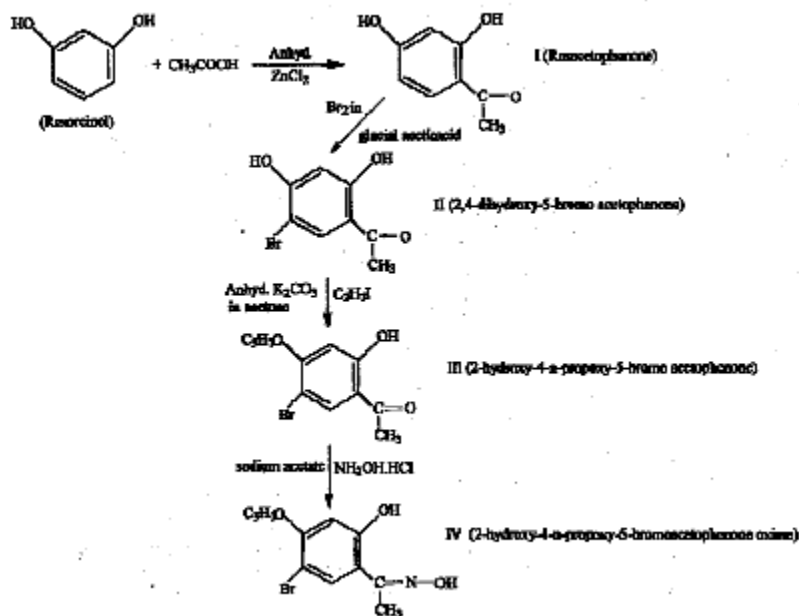
Frequency	HnPBAO	HnPBAPT
v(N-O)	970	-
v(O-H)	3400	3300
v(C=N)	1640	1640
v(C-O) >C-OH	1150	1310
v(C=S)	-	1220
v(N-N)	-	1165
v(C-Br)	560	560
v(R-O-R')	1200 and 1030	1290 and 1070

Table 3: UV-Visible spectra of HnPBAO in ethanol and HnPBAPT in DMF

Reagents	Wavelength of maximum absorbance (nm)
HnPBAO HnPBAPT	233.0, 265.0, 306.0218.0, 275.0, 326.0

The reactions for the synthesis of HnPBAO are given in scheme 1.

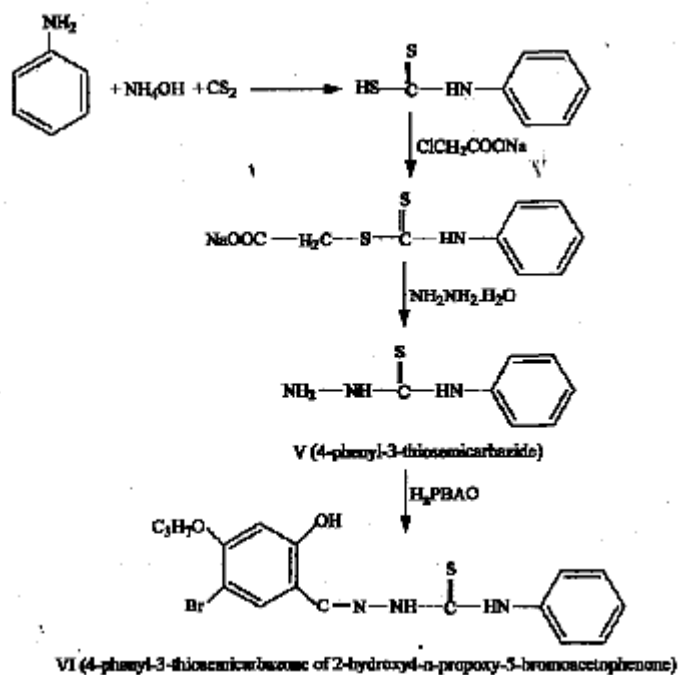
Synthesis of 4-phenyl-3-thiosemicarbazone of 2-hydroxy-4-n-propoxy-5-bromoacetophenone(HnPBAPT).



Scheme 1:

4-phenyl-3-thiosemicarbazone was obtained by the method used by Kazapov and Postovskil [9]. According to the stated procedure, Aniline (0.1 mole) was dissolved in ethanol (approx 30 ml) and NH_4OH (1:1, 20ml) was added to it. The reaction mixture was cooled below 30°C (i.e room temperature) and CS_2 (8ml) was added slowly with rigorous stirring and cooling. After complete dissolution of CS_2 , the solution was allowed to stand

for one hour and then added to 4ml aqueous solution of sodium salt of monochloroacetic acid. During condensation the mixture was heated till the colour changed from red to yellow. To the warmed solution, 50% hydrazine hydrate (10ml) was added with stirring. The mixture was filtered and the filtrate was evaporated to half the quantity. It was then allowed to stand overnight. The product obtained was 4-phenyl-3-thiosemicarbazone[V].



Scheme 2:

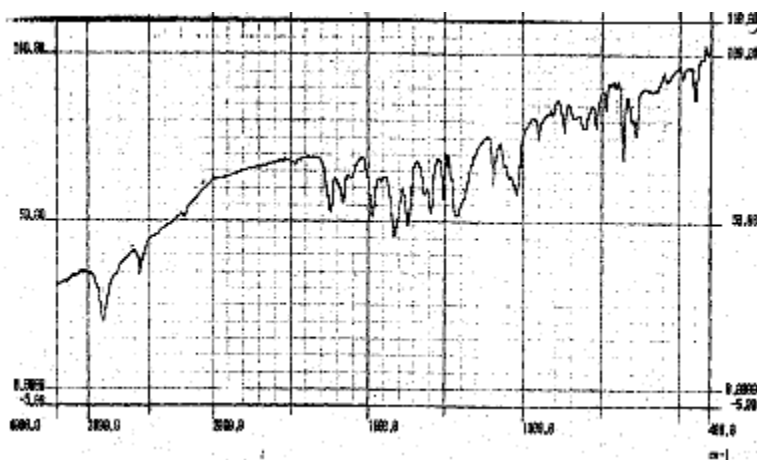


Fig 1: IR spectra of HnPBAO

A mixture of compound [IV] (2.73gm, 0.01mole), V (1.67gm) and hydrochloric acid (3ml) in ethanol (30ml) was refluxed for 4 hours. The mixture was then poured on ice-cold water. Orange solid thiosemicarbazone separated out. This was then filtered, washed and crystallized from ethanol. Yellowish orange crystals were obtained having m.p ($160 \pm 1^\circ\text{C}$), known as 4-phenyl-3-thiosemicarbazone of 2-hydroxy-4-n-propoxy-5-bromoacetophenone (HnPBAPT). The reactions for the synthesis of HnPBAPT are given in scheme 2.

RESULTS AND DISCUSSION

The physical data for the reagents are listed in Table-1. Both reagents obtained were coloured crystals. HnPBAO was soluble in ethanol, while HnPBAPT was found to be sparingly soluble in many organic solvents like CCl_4 , CHCl_3 , Ethylacetate, Ethanol etc. and soluble in DMF. Reagent solution of HnPBAO was prepared in ethanol for gravimetric study, whereas for spectrophotometric studies the solution for both HnPBAO and HnPBAPT was prepared in DMF. The reagent solution was found to be stable for three days.

Both reagents were analysed for its carbon, hydrogen and nitrogen content and the results obtained are tabulated in table-1. A perusal of table-

I reveals that, the percentage of elements is found to be in agreement with its molecular formula (calculated value).

The important IR spectral data of both ligands are given in table-II. The IR spectra of HnPBAO (Fig 1) shows two band for O-H stretching. One band at 3400 cm^{-1} is due to phenolic -OH group and the other at 2970 cm^{-1} is due to oximino group. A peak at 1640 cm^{-1} observed is due to the $>\text{C}=\text{N}$ stretching. Two peaks at 1200 cm^{-1} and 1030 cm^{-1} are due to C-O-C ether stretching. A peak seen at 560 cm^{-1} is due C-Br stretching. A peak at 1150 cm^{-1} is due to C-O stretching of phenolic C-OH. A peak at 970 cm^{-1} is due to N-O Stretching.

IR spectra of HnPBAPT (Fig 2) shows a peak at 3300 cm^{-1} due to OH stretching. A peak at 1640 cm^{-1} is due to $>\text{C}=\text{N}$ stretching. A peak at 1310 cm^{-1} is due to $>\text{C}-\text{O}$ stretching of $>\text{C}-\text{OH}$ aromatic group. The peaks at 1290 cm^{-1} and 1070 cm^{-1} are due to aromatic ether R-O-R' stretching (R' is alkyl group). A peak at 750 cm^{-1} and 560 cm^{-1} is due to C-H bending of phenyl and C-Br stretching respectively.

The UV-Visible spectra of the reagent HnPBAO in ethanol and HnPBAPT in DMF is given in Table 3 and the graphs are shown in Fig 3.1 -3.2.

From the above studies, it is clear that both

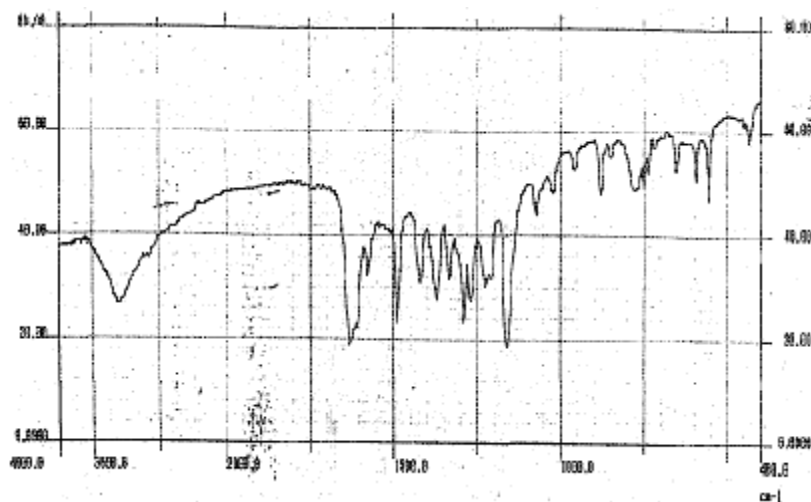


Fig. 2: IR spectra of HnPBAPT

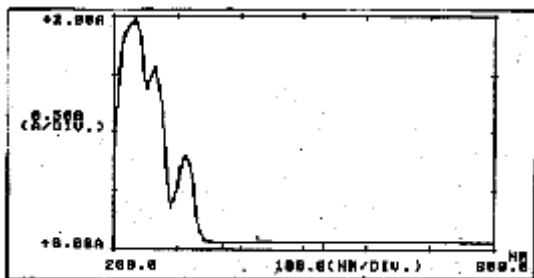


Fig. 3.1: Absorption spectra of HnPBAO

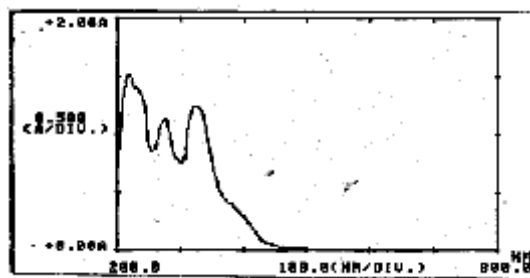


Fig. 3.2: Absorption spectra of HnPBAT

ligands offer good sensitivity and selectivity for the further study of metal ligand complexes.

CONCLUSIONS

The ligand HnPBAO offers quite a good number of advantages, as stated below:

1. The reagent HnPBAO is light green solid and forms good stable complexes with metal ions.
2. The ligand has high molecular weight and due to higher conversion factor, small quantity of metal ion can be determined with more accuracy in gravimetric analysis.
3. Many cations and anions do not interfere in the spectrophotometric determination of metal ions using the above mentioned reagent.

4. The ligand or reagent is suitable for determining metal content in ores and alloys.

The ligand HnPBAPT is found to have potentiality as an analytical tool due to following reasons.

1. It forms intense coloured complexes with metal ions due to a strong chromophoric system.
2. Due to -OH groups in ortho position, chelate formation is facilitated. This leads to formation of more stable complexes.
3. The complexes formed with HnPBAPT do not decompose in few hours.
4. HnPBAPT can also be used in pharmaceutical industries for the determination of FeIII. in pharmaceutical samples.

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