

## 2-Hydroxy-4-Isopropoxy-5-bromoacetophenone Oxime as An Analytical Reagent for Palladium(II) Determination

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**Abstract:** 2-Hydroxy-4-isopropoxy-5-bromoacetophenone oxime (HIBAO) has been synthesized and used as an analytical reagent for gravimetric and spectrophotometric determination of Pd(II). In pH range of 2.0 to 6.0 this reagent gives water insoluble yellow coloured complex with Pd(II). The reagent has been used for gravimetric determination of Pd(II). Interference of many cations and anions in gravimetric determination is studied for respective metals. Metal to ligand ratio of the complex has been determined using spectrophotometric methods. The stoichiometry of Pd(II) complex is 1:2 [M:L]. The complex obeys the Beer law up to 53.21 ppm of Pd(II). The molar absorptivity and Sandell's sensitivity of the complex have also been calculated. The stability constant and Gibb's free energy change at 300 K are reported. Applicability of the reagent has been checked by determining palladium in palladised carbon. The IR spectra of ligand and complex has also been studied to establish the nature of linkage of metal ion with ligand.

**Keywords:** Oxime, Analytical reagent, 2-Hydroxy-4-isopropoxy-5-bromoacetophenone oxime, HIBAO, Palladium (II)

### Introduction

In the current scenario of analytical chemistry, many organic reagents are widely used as analytical reagents. They include *o*-hydroxy ketoximes<sup>1-7</sup>, phenyl hydrazones, thiosemicarbazones<sup>8-10</sup>, chalconeoximes<sup>11</sup> etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. On reviewing literature, it was found that the bromo derivative of *o*-hydroxy ketoximes has not been used much. Further study of palladium(II) ion is less reported. With the introduction of bromine, the molecular weight of reagent is increased, which is expected to give advantage of higher conversion factor. Here we report the use of 2-hydroxy-4-isopropoxy-5-bromoacetophenone oxime as an analytical reagent for Pd(II).

### Experimental

All the spectrophotometric work, pH measurements and elemental analysis were done on Shimadzu UV-160A, UV-Visible spectrophotometer, Equip-tronic pH meter (EQ-614) and Carlo Erba elemental analyzer respectively. Mettler electronic single pan balance AE-163 was used for weighing. The IR spectra were recorded on "Perkin-Elmer" FTIR Spectrophotometer (RX-1).

### *Synthesis of HIBAO*

Resacetophenone was synthesized from resorcinol, acetic acid and anhydrous zinc chloride according to the method of Robinson R and Shah R. C<sup>12</sup>. 2,4-dihydroxy-5-bromoacetophenone was obtained by brominating resacetophenone with bromine in glacial acetic acid. 2-hydroxy-4-isopropoxy-5-bromoacetophenone was prepared by condensation of 2,4-dihydroxy-5-bromoacetophenone and isopropyl bromide in acetone and anhydrous potassium carbonate. The ketone was converted to oxime by usual method using hydroxylamine hydrochloride and sodium acetate. The oxime was recrystallised from ethanol. White coloured crystals with m.p.195 °C. (Nitrogen found: 5.02%, Calculated :4.86%)

### **Results and Discussion**

#### *Gravimetric determination of Pd(II)-HIBAO complex*

A 0.04 M solution of the reagent in 60% aqueous ethanol were used for gravimetric analysis of Pd(II). Palladium chloride (0.01 M, 20 mL) solutions were taken in clean beakers and diluted to about 100 mL with distilled water and pH of the solutions were adjusted using suitable buffer. The solutions were warmed to 60 °C and a small excess of reagent (0.04 M, 11 mL) was added. The yellow coloured precipitate obtained were digested on water-bath for 60 minutes at 60 °C. The precipitate were filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by 60% aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110 -115 °C in hot air oven, cooled and weighed. The experiment was repeated with different aliquots, keeping the optimum pH to evaluate its applicability. The reagent works satisfactorily for gravimetric determination of Pd(II) in pH range 2.0 to 6.0. Error in any case did not exceed  $\pm 1.0\%$ .

#### *Interference*

To study the effect of foreign ions in gravimetric determination, 8 10 mg of various cations were added to solution containing 21.28 mg Pd(II) at pH 5.0 and gravimetric estimations were done as described earlier. It was observed that cations like Ca(II), Mg(II), Ni(II), Mn(II), Zn(II), Sr(II), Cd(II), Ba(II), K(I) and Na(I) do not interfere at pH 5.0 during the gravimetric analysis of Pd(II) but Fe(III), Cu(II), Co(II) and V(V) interfere seriously. Interference due to Fe(III) can be removed by masking with fluoride ion. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

#### *Spectrophotometric study of Pd(II)-HIBAO complex*

It was found that Pd(II)-HIBAO complex is soluble in ethyl acetate, chloroform and DMF. To have the absorption spectra, 5 mg of complex was dissolved in 25 mL of ethyl acetate and absorption spectra of this solution was recorded in the wavelength range of 350 nm to 600 nm. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. All the measurements were carried out at 400 nm.

To verify the Beer law different aliquots of Pd(II) solution(0.005 M) were taken and buffer solution of CH<sub>3</sub>COOH + CH<sub>3</sub>COONa was added to maintain pH 5.0. The excess of reagent (0.01 M,6.0 mL) was added to get precipitate of complex. It was extracted with three 5.0 mL portions of ethyl acetate and the combined extracts were diluted to 25 mL. The absorbances of these solutions were measured at 400 nm against reagent blank. The absorbances were plotted against the concentration of Pd(II). It was found that Beer's law is obeyed up to 53.21 ppm of Pd (II). The molar absorptivity and Sandell's sensitivity were

calculated from Beer's law plot and were found to be  $1.124 \times 10^3 \text{ L.mol}^{-1}.\text{cm}^{-1}$  and  $0.095 \mu\text{g}$  of Pd(II)/ $\text{cm}^2$  respectively. Job's<sup>13</sup> and Mole-ratio<sup>14</sup> methods were used to determine the stoichiometry of the complex. It was found to be 1:2 [M: L].

#### *Stability constants from Job's method and mole-ratio method*

The stability constants were calculated using the formula,

$$K_s = \frac{1-\alpha}{4\alpha^3 c^2} \quad \text{Where, } \alpha = \frac{E_m - E_s}{E_m}$$

Where,  $\alpha$  = Degree of dissociation

$E_m$  = Maximum absorbance obtained at the intersect of the two lines.

$E_s$  = Absorbance at the stoichiometric molar ratio of the metal to ligand in complex. The average stability constant obtained from two methods is  $9.54 \times 10^9$ . From mean  $K_s$  value, the standard free energy change  $\Delta G^0$  at 300 K for the formation reaction of complex has been calculated using the formula.

$$\begin{aligned} \Delta G^0 &= -RT \ln K_s \\ &= -13.70 \text{ K.cal/mole} \end{aligned}$$

#### *IR spectra*

The IR spectrum (in KBr pellet) of ligand shows two bands for O-H stretching. One band at  $3407 \text{ cm}^{-1}$  is due to phenolic 2-OH group and the other at  $3300 \text{ cm}^{-1}$  is due to oximino -OH group. A peak observed at  $1636 \text{ cm}^{-1}$  is due to the  $>\text{C}=\text{N}$  stretching. A peak at  $1221 \text{ cm}^{-1}$  is due to C-O-C ether stretching. The peaks at  $1028 \text{ cm}^{-1}$  and  $645 \text{ cm}^{-1}$  are observed due to N-O stretching and C-Br stretching respectively. Examination of the IR spectra of the chelate shows that the band due to O-H stretching of 2-hydroxy group disappears in a complex. This indicates that during chelate formation, the hydrogen of 2-hydroxy group is lost and oxygen forms covalent bond with metal. The absorption band observed due to  $\text{C}=\text{N}$  stretching at  $1636 \text{ cm}^{-1}$  in ligand is shifted towards shorter wave number at about  $1620$  to  $1625 \text{ cm}^{-1}$  in the complex. This indicates that metal is coordinately bonded with nitrogen. This is also supported by slight downward shift of  $\nu_{\text{NO}}$  from  $1028 \text{ cm}^{-1}$  in ligand to  $950 \text{ cm}^{-1}$  in complex. The other bands due to oximino O-H stretching, C-O-C ether stretching and C-Br stretching observed in ligand are unaffected in spectrum of complex. Thus the comparison of IR spectra of ligand with that of complex indicates that metal is covalently bonded with oxygen and coordinately bonded with nitrogen of oximino nitrogen.

#### *Determination of palladium in palladised carbon*

The sample of palladised carbon 2.8466 g was weighed exactly and dissolved in concentrated nitric acid. The solution was heated to remove excess of acid and finally the solution was diluted to 250 mL. 50 mL of the above solution was taken in a clean 250 mL beaker and palladium was determined gravimetrically using HIBAO as per the procedure described previously. The results were compared with the percentage of palladium determined using dimethyl glyoxime, a standard method to estimate palladium. Percentage of Pd found using HIBAO 4.95% (Average of three determinations); Percentage of Pd found using DMG 4.92%.

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