



2, 4-Dihydroxy-5-Bromo [2'Methyl] Propiophenone Thiosemicarbazone [DHBMP] as an Analytical Reagent: Studies on Pd (II) Chelate

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Abstract : 2, 4-Dihydroxy-5-Bromo-[2'methyl]-Propiophenone thiosemicarbazone [DHBMP] has been used for the spectrophotometric determination of Pd(II) at pH = 2.5. Job's method of continuous variation and Yoe and Jones Mole ratio method show metal: ligand ratio in the complex to be 1:1. The molar absorptivity of complex at 390 nm was found to be 1.457×10^3 $\text{lit.mol}^{-1}.\text{cm}^{-1}$ and Sandell's sensitivity was found to be $0.0730 \mu\text{g}/\text{cm}^2$. The stability constant determined spectrophotometrically is found to be 1.35×10^6 and Gibb's free energy change for complex formation reaction is calculated to be $-8.414 \text{ k.cal/mole}$. The Beer law is obeyed up to 7.45 ppm of Pd (II) ion at 390 nm. From TG studies, the energy of activation for both the decomposition steps has been calculated using broido method. They were found to be 23.04 k.cal/mole and 3.1 k.cal/mole respectively. The reagent has been successfully applied for the determination of percentage purity of palladium from palladiated carbon sample.

Introduction

In the current scenario of analytical chemistry, large numbers of organic reagents have been employed for the detection of metal ions. The thiosemicarbazone of aromatic aldehydes and ketones have been used as spectrophotometric reagent for different metal ions. It is found to be better chelating agents and they have been exploited to the maximum extent by many workers⁽¹⁻⁷⁾. Many organic reagents like oximes, thiosemicarbazones, chalconeoxime, anilides, various heterocyclic compounds have been used for gravimetric and spectrophotometric reagent for Pd (II). Spectrophotometric methods have been used to confirm the stoichiometry of the complex and to determine the stability constant of the complex. The stoichiometry was also confirmed by thermo gravimetric analysis. Here, we report the use of 2, 4-Dihydroxy-5-Bromo-[2'methyl]-Propiophenone thiosemicarbazone [DHBMP] as a spectrophotometric reagent for Pd (II).

Experimental

Instruments

Spectrophotometric measurements were done on Perkin-Elmer Lambda-35 UV-Visible spectrophotometer and all the pH measurement were done on electronic pH-meter (EQ-614). TG analysis was done using "Mettler-Instrument STAR SW11.00".

Reagent and Solutions

Pd (II)-metal solution: A stock solution of Palladium (II) (0.01M) was prepared by dissolving 0.4435 gm of palladium chloride (A.R. Grade) in concentrated hydrochloric acid and diluting with deionized water to 250ml. It was standardised with DMG ⁽⁸⁾.

Solutions of other ions were prepared by dissolving their salts (A.R) in deionized water.

Synthesis of Reagent [DHBMP]:

2, 4 dihydroxy [2'methyl] propiophenone (DHMP) was prepared from resorcinol, phenyl acetic acid and anhydrous zinc chloride according to the method of H.Nogemi ⁽⁹⁾. 2, 4-dihydroxy-5-bromo [2'methyl] propiophenone (DHBMP) was prepared from 2, 4 dihydroxy [2'methyl] propiophenone (DHMP) and bromine in glacial acetic acid. It was crystallized from ethanol. The reagent was prepared by the reaction of 2, 4-dihydroxy-5-bromo [2'methyl] propiophenone with alcoholic solution of thiosemicarbazide. The reagent was crystallized from absolute alcohol having m. p. 123°C.

Characterization of Reagent

The thiosemicarbazone reagent under present investigation is characterized by following different analytical techniques.

Elemental analysis: Elemental analysis of the reagent was done using "Carlo-Erba Elemental Analyzer Model 1106". The percentage elements, found are in agreement with its molecular formula. The results are given in the following Table-I.

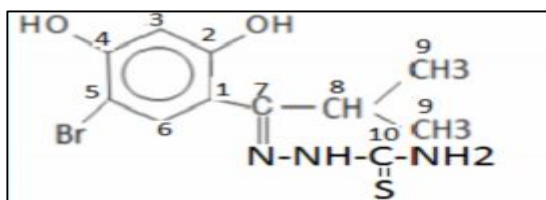
TG Studies: The Thermo Gravimetric study of Chelate was done on "Mettler-Instrument STAR SW11.00".

UV-Visible spectral studies: The UV-Visible spectrum of reagent in ethanol was recorded on Perkin-Elmer Lambda-35 UV-Visible spectrophotometer. Wavelengths of maximum absorptions were found to be 222, 268 and 337 nm that falls in UV region.

FT-IR Spectral studies: FT-IR spectrum of the reagent and its chelate was recorded on "Simadzu 8400-S spectrophotometer" in KBr pallet. Absorption bands observed are shown in Table-II.

¹H and ¹³C NMR Spectral Studies:

The NMR spectrum of the reagent was taken in CDCl₃. The NMR spectrum was recorded on a BRUKER AVANCE II 400 NMR spectrometer using TMS as reference. Assignment of signals to different protons and carbons are given in Table-III and Table-VI.



2, 4-Dihydroxy-5-Bromo-[2'methyl]-Propiophenone thiosemicarbazone [DHBMP]

Result and Discussion

Antibacterial activity of reagent and chelate:

Thiosemicarbazones being chelating agent's shows good antibacterial activity ⁽¹⁰⁻¹²⁾ by hinder the growth of bacteria by chelating the metal ions which are present in trace in biological fluids. The antibacterial properties of the above compound are studied by using "Broth Dilution Method" ^(13, 14). The results are given in Table.

Standard Drugs	E.Colli / gram -ve / microgram/ml	S.Aures / gram +ve / microgram/ml
GENTAMYCINE	0.05	0.25
AMPICILINE	100	250
CHLORAMPHENICOL	50	50
CIPROFLOXACIN	25	50
NORFLOXACIN	10	10
SAMPLE	E.Colli / gram -ve / microgram/ml	S.Aures / gram +ve / microgram/ml
DHBMPT	250	125
Pd(II) - DHBMPT	125	250

DHBMPT reagent shows poor activity against E.coli (Gram-ve) bacteria while shows good activity for S. Aureus (Gram+ve) bacteria which is more than “Ampicilline Drug”.

Pd(II) -DHBMPT Chelate shows good activity against E.coli (Gram -ve) bacteria while exhibit same activity against S. aureus (Gram +ve) bacteria which is same as “Ampicilline Drug”.

Spectrophotometric study of Pd (II) -DHBMPT

5 mg of chelate was dissolved in 25ml of (50% v/v) aqueous ethanol and the absorption was recorded in the range of 340 -800 nm. It was observed that the absorbance of the coloured solution of the chelate increase continuously towards the shorter wavelength. The spectra of chelate shows shoulder band at 390 nm and this wave length was selected for further spectrophotometric work. pH study of chelate from pH=1.0 - 4.0 was done using appropriate buffer and maximum absorbance was observed at pH=2.5. Hence this pH was selected for further spectrophotometer work.

Verification of Beer's law and optimum concentration range

To 4.0ml (0.002M) solution of DHBMPT reagent varying amount of the palladium ion solution (0.0005M) was added and pH was maintained 2.5 using hydrochloric acid and sodium acetate .Then dilute it to 25ml with (50% v/v) aqueous ethanol. Absorbance of this solution was measured at 390 nm against ligand blank. Absorbances were plotted against concentration of Pd (II). A straight line passing through the origin, indicating the obeyence of the Beer law was obtained up to 7.45 ppm of Pd (II). The molar absorptivity and Sandell's sensitivity⁽¹⁵⁾ were found to be $1.457 \times 10^3 \text{ lit. mol}^{-1} \cdot \text{cm}^{-1}$ and $0.0730 \mu\text{g/cm}^2$ respectively.

Stoichiometry of complex

Job's method⁽¹⁶⁾ and Mole ratio method⁽¹⁷⁾ were used to determine the stoichiometry of the Pd(II)-DHBMPT complex. From both the It was found to be 1:1[M: L]. This is in agreement with the stoichiometry found from thermogravimetric method .

$$K = \frac{1-\alpha}{4\alpha^3 C^2}, \text{ where } \alpha = \frac{E_m - E_s}{E_m}$$

Where, α = degree of dissociation

E_m = maximum absorbance found from graph.

E_s = absorbance at the stoichiometric molar-ratio of the metal to reagent in complex.

C = concentration of complex

The average stability constant from two method is 1.35×10^6 and Gibb's free energy change for complex formation reaction was calculated using the formula $\Delta G^\circ = -RT \ln K_s$ found to be $-8.414 \text{ k.cal.mol}^{-1}$ at 27°C.

Effect of diverse ion:

Interference due to associated ions was examined in the determination of 7.45 ppm of Pd (II) at pH- 2.5 using the reagent DHBMP. The tolerance limit was taken as the amount of foreign ion required to cause $\pm 2\%$ error in the absorbance.

Many anions like F^- , Cl^- , Br^- , NO_3^- , and SO_4^{2-} do not interfere in the determination of Pd (II) at pH-2.5, even when they are present in 100-fold excess. Sr(II), Ca(II), Mg(II), Cd(II), Na(I), K(I), Ba(II) and Zr(IV), do not interfere when they are present up to 10-fold excess.

Thermo gravimetric analysis:

Thermo gravimetric analysis of Palladium chelate was done on "Mettler-Instrument STAR SW 11.00". A definite quantity of chelate was taken in an alumina crucible and was put on a hanger of microbalance and crucible was kept in a furnace. The temperature of the furnace was raised from 30°C to 900°C in a programmed manner at the heating rate of 10°C/min.

From thermo gravimetric analysis of the Pd(II) chelate, it was found that there is no mass loss up to 160°C, indicating that the chelate can be dried safely without decomposition at 160°C. Loss in mass above 160°C is due to decomposition of chelate and loss of ligand molecules. Mass of final residue corresponds to Pd metal is in accordance with the formula $(C_{11}H_{13}O_2N_3SBr)$ Pd. The observed loss and mass expected as per formula of chelate in which M: L ratio is 1:1 in the complex. Broido method⁽¹⁸⁾ was applied to TG thermo grams of Pd(II) chelate obtained with heating rate 10°C/min. Activation Energy E_a was calculated using this method for thermal decomposition of chelates. The value of ' E_a ' was found to be 23.04 and 3.1 k.cal/mole for first and second decomposition step respectively.

IR Spectra:

Examination of IR spectra of the chelate shows the weak band around 3384 cm^{-1} in comparison of ligand molecule, which shows that during chelate formation, the hydrogen of 2- hydroxy group is lost and oxygen forms covalent bond with metal whereas 4- hydroxy group does not take part in complex formation. The bands of aliphatic C-H stretching and aromatic C-H stretching are observed at nearly same position in reagent as well as in palladium complex. The band due to C=N stretching which is observed at 1618 cm^{-1} in ligand is shifted to around 1585 cm^{-1} in complex. This may be due to coordination of palladium metal through nitrogen. Thus, in the chelates, metal is covalently bonded with oxygen and co-ordinately bonded with nitrogen.

Table-I: Elemental analysis of reagent DHBMP

Reagent	%Carbon [Calc.]	%Hydrogen [Calc.]	%Nitrogen [Calc.]	%Sulphur [Calc.]
DHBMP	39.80% [39.77%]	4.18% [4.25%]	12.58% [12.65%]	9.61% [9.65%]

Table-II: FT-IR Spectral studies of reagent DHBMP

Reagent	ν^{O-H} stretching	$\nu^{C=N}$ stretching	ν^{C-H} stretching	$\nu^{C=S}$ stretching	ν^{C-Br} stretching	ν^{N-N} stretching
DHBMP	3384 cm^{-1}	1618 cm^{-1}	2875-2972 cm^{-1}	1273 cm^{-1}	650 cm^{-1}	1136 cm^{-1}

Table-III: ¹H-NMR

Reagent	-CH ₃ Alkyl group	Methine proton	Phenolic (-OH)	-NH ₂ Proton	-CSNH Proton	Aromatic Proton
DHBMPT	Doublet δ = 1.30	Multiplate δ = 2.20	Singlet δ = 13.51, 13.32	Singlet δ = 4.17	Singlet δ = 12.72	Multiplate δ = 6.4 to 8.00

Table-VI: ¹³C-NMR

Assignment	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Chemical shift(δ) In ppm	113.70	155.66	103.67	155.66	99.38	130.39	161.58	55.31	44.01	201.87

Applied Work

Spectrophotometric determination of Palladium in Palladiated Carbon.

The sample of palladiated carbon (1.0035 gm) dissolved in concentrated nitric acid by heating on a sand bath. It was heated till little amount of acid was left. Similar treatment was given 2-3 times. The solution was heated on a sand bath to remove excess of acid and the solution was diluted to 250 ml with double distilled water in a volumetric flask.

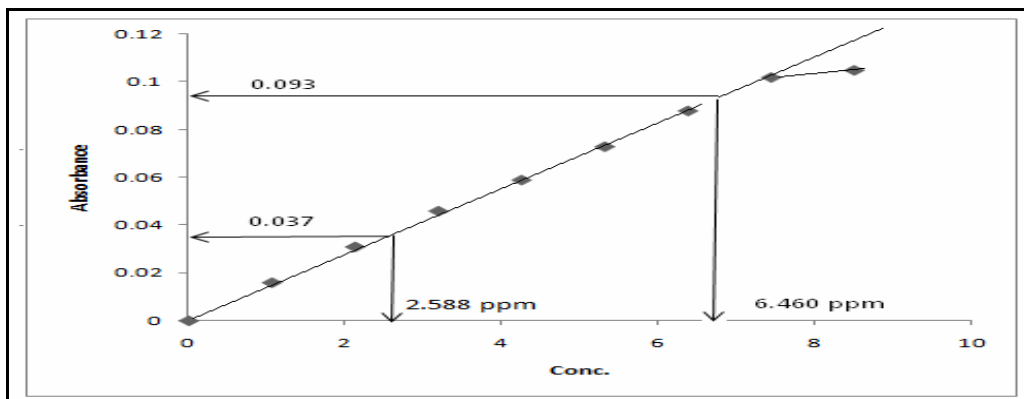
From this 250 ml solution, 20.0 ml solution was taken and again diluted with double distilled water to 1000 ml stock solution (1ml = 2.6 μg).

An aliquot of the above diluted solution 1.0 ml and 2.5 ml was pipette out in a 50 ml beaker. To this solution excess ethanolic solution of reagent DHBMPT was added and the pH was adjusted to 2.5 with buffer. The solution was diluted to the 25ml mark with aqueous ethanol as to keep 50% concentration of ethanol in final diluted soln. Absorbance of above solutions were measured at 390 nm using ligand blank.

Reported percentage of Pd(II) in palladiated carbon sample = 3.22 %

Absorbance	ppm of Pd(II) taken	ppm of Pd(II) found	percentage of Pd(II) obtained	%Error
0.037	2.60	2.588	3.205	-0.47
0.093	6.50	6.460	3.200	-0.62

Applied work for Pd(II) in paladised carbon sample



Absorbance values obtained were plotted in Beer's law plot.

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References

1. A.werner-Z. Anorg.Chem.,3, 270(1893) .
2. D. Prem Kumar, A. Praveen Kumar and P. Raveendra Reddy Research Journal of Chemical Sciences a. ISSN 2231-606X Vol. 5(2), 4-7, February (2015).
3. D. Prem Kumar, A. Praveen Kumar, P. Saifulla Khan and P. Raveendra Reddy Int. Journal of Analytical and Bioanalytical Chemistry; 5(3): 61-64 (2015).
4. G. Sreenivasula Reddy and P. Raveendra Reddy J. Mater. Environ. Sci. 6 (6) 1699-1708 ISSN: 2028-2508(2015).
5. K. P. Sateesh, V. Suryanarayan Rao Journal of Advanced Scientific Research J Adv Sci Res 6 (2): 14-17 (2015).
6. Shobha S. Borhade International Journal of Recent Trends in Science And Technology, ISSN 2277-2812 E-ISSN 2249-8109, Vol.10, 3, pp 423-429(2014).
7. M.Hymavathi, N.Devanna and C.Viswanatha World Journal of Pharmacy and Pharmaceutical Sciences Vol 3, Issue 8, (2014).
8. Idem., Ibid. 4th Ed., P.463.
9. H. Nogami; J. Pharm.Soc., Japan, 61, 46(1945).
10. S. R. Modi Ph. D. Thesis, South Gujarat University, Surat (1994).
11. S. H. Abo EL Fetoh, A. E. Eid, A.T. Abd EL-Kareem and M. A.Wassel; J. Mater. Sci. Technol., Vol. 14(1998).
12. A. K. Parekh and K. K. Desai; Indian J. Chem., Vol. 45B pp. 1072-1075 (2006).
13. Clinical Microbiology procedure handbook, vol. II, chapter 5, Page no. 501, Henry d. Isenberg, 2nd edition.
14. Indian Journal of chemistry, section-b, vol.46b, pp. 550-553 (2007).
15. E. B.sandell "Colourimetric determination of traces of metals" 3rd., Wiley Inter science (1962).
16. P. job; Ann(10),9,113(1928);(11),6,97(1936); compt. Rend., 180,928(1925) .
17. J. H. Yoe and A. L. Jones; Ind.Engg.chem.Anal.Ed, 16,111(1944) .
18. A. Broido; J. Polymer Sci., Part A-2, 7, 1761 (1969).
