

NOTES

3-Hydroxy-3-Methyl-1-*o*-Carboxy Phenyl Triazene: A New Reagent for Spectrophotometric Determination of Palladium

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The work describes the application of 3-hydroxy-3-methyl-1-*o*-carboxy phenyl triazene as spectrophotometric reagent for palladium.

3-Hydroxy-3-methyl-1-*o*-carboxy phenyl triazene has been reported for gravimetric determination¹ of Ti(IV), spectrophotometric determination² of Fe(III), Ti(IV) and V(IV). In the present paper the utility of this reagent in spectrophotometric determination of Pd(II) is being reported.

Palladium(II) forms a yellow 1 : 1 (Pd : R) complex with the reagent (six fold molar excess) and has λ_{max} at 378 nm. The colour develops instantaneously. For constant maximum absorbance, the metal to reagent ratio 1 : 6 is taken, and pH is found between 2.00 to 2.65.

Beer's law is obeyed over the concentration range $0.2 \times 10^{-4} \text{M}$ to $1.2 \times 10^{-4} \text{M}$ of palladium. Using Job's method, mole ratio method of Yoe and Jones and Zolotov's mole ratio method the molar composition of palladium complex with the reagent is found as 1 : 1. The molar absorptivity, and Sandell's sensitivity at 378 nm are $7,500 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and 14.19 ng/cm^2 . For 10.64 ppm of palladium standard deviation (ten measurements) was found as 0.043 ppm (0.40%). The stability constant of the complex was determined by Harvey and Manning's method³ (using Mole Ratio Curve) and Purohit's method⁴ (using Job's Curves). Using the above methods the value of $\log \beta$ were found as 7.033 and 6.967 respectively.

The reagent was synthesised as per the reported method¹. The greyish shining crystals had the melting point 186°C .

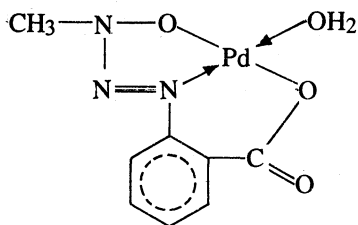
Procedure: In a 10 ml volumetric flask appropriate volumes of palladium and reagent solutions were taken such that the metal to reagent ratio is 1 : 6 and the solvent is water : ethanol (60 : 40 v/v) in the final solution. The pH was adjusted between 2.0 to 2.65. The colour formation is instantaneous and is stable for at least 24 h. The absorbance was measured against reagent blank at 378 nm. Prepared a calibration curve accordingly.

The composition of the complex was found to be 1 : 1 (Pd : R) with the help of Job's⁵, Mole Ratio method of Yoe and Jones⁶, Zolotov's mole ratio method⁷ and Slope Ratio method⁸. Further, the Slope Ratio method of course gives the

composition 1 : 1 but when metal is present in excess the absorbance is more than expected. Similarly in Zolotov's mole ratio method also, the constant maximum absorbance value is higher than the expected value. These increases have been explained subsequently.

Preparation of Solid Complex: The molar proportion of palladium chloride dissolved in minimum quantity of conc. HCl and reagent solution in alcohol at desired pH are mixed and the solid complex was obtained. The yellowish orange complex has melting point 240°C and molecular formula $\text{Pd}(\text{C}_8\text{H}_7\text{N}_3\text{O}_3)\text{H}_2\text{O}$ as revealed by elemental analysis and thus tends support to the composition found by solution studies.

The ligand has the presence of carboxy group in *ortho* position on the 1-phenyl ring and would act as dibasic tridentate ligand. The 1 : 1 palladium complex may tentatively be assigned the following square planar structure:



(I)

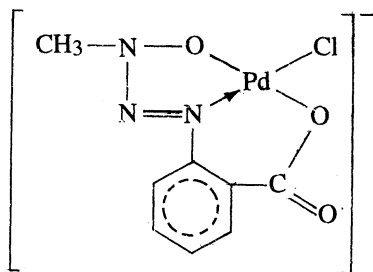
The presence of water molecule is indicated by the elemental analysis of the solid complex.

IR spectral studies of both the reagent and the solid palladium complex have been made. The comparison reveals that ν_{NH} 3030 cm^{-1} (m), δ_{NOH} 1095 cm^{-1} (m), δ_{NH} 1500 cm^{-1} (w) and ν_{OH} ($-\text{COOH}$ group) 3220 cm^{-1} (m) bands of the hydroxytriazenes have disappeared in the spectra of corresponding palladium complex. The ν_{OH} band was not observable in the spectra of ligand.

Further, a strong band is observed in the spectra of palladium complex at 3175 cm^{-1} (s) which may be assigned as ν_{OH} band (due to presence of water molecule). The position of $\nu(\text{C}=\text{O})$ in the ligand is observed at 1680 cm^{-1} (s) and in complex the position of $\nu(\text{C}=\text{O})$ band is lowered to 1615 cm^{-1} (w) for obvious reasons.

It was pointed out earlier that in case of Slope Ratio method and Zolotov's mole ratio method the absorbance is more than expected, when metal is present in excess. It is obvious that with increase in palladium concentration the HCl concentration also increases. As the concentration of HCl increases it is very likely that the H_2O present (structure I) is replaced partially or wholly by a chloro group giving another species as structure-II.

Might be, this negatively charged species has a higher absorbance as compared to the aquo species. Thus, the actual absorbance observed may either be exclusively



(II)

due to species(II) or due to both the species if the aquo molecule has not been replaced completely by chloro group.

Effect of Diverse Ions

It was found that Hg(II), Zn(II), Mn(II), Cd(II), Co(II), Sn(II), F⁻, Br⁻, CH₃COO⁻, NO₂⁻, oxalate, CO₃²⁻ and tartrate interfere at 5 ppm level in the determination of 10.64 ppm of palladium. However, 10.64 ppm of palladium can be determined in presence of 5 ppm of either of the ions K(I), Na(I), NH₄(I), Ba(II), Ni(II), Mg(II), Cr(III), Th(IV), molybdate, Cl⁻, I⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ or 100 ppm of either of the ions K(I), Na(I), NH₄(I), Ni(II), molybdate, Cl⁻, NO₃⁻ and PO₄³⁻.

Sandell's sensitivity

Sandell's sensitivity (ng/cm²) of the proposed reagent along with the sensitivity of some reagents reported for the spectrophotometric determination of palladium are:

3-Acetoxy-7-methyl phenothiazine⁹ (15.0); benzyl dimethyl phenyl ammonium [benzyl dimethyl anilinium] chloride¹⁰ (20.0); thioridazine hydrochloride¹¹ (24.0); pot. ethyl xanthate¹² (580); pot. propyl xanthate (600.0); pot. butyl xanthate (650); pot. benzyl xanthate (500); pot. isoamyl xanthate (500); 4, 4, 6-trimethyl-1-phenyl (1H, 4H)-pyrimidine-2-thiol¹³ (26.0); 3-hydroxy-3-methyl-1-*o*-carboxy phenyl triazene (14.19).

Thus the proposed reagent is more sensitive as compared to the nine other reagents as shown above.

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