REACTION OF PALLADIUM(II) CHLORIDE WITH ACRIFLAVINE, A NEW SPOT TEST FOR PALLADIUM(II)

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SUMMARY

New micro- and spot-test procedures are described for the detection of Pd(II), using the common antiseptic dye acriflavine as the reagent. A drop of test soln. when mixed with a drop of 0.1 percent aq. dye soln. on an ordinary filter paper, a more or less deep orange spot surrounded by yellow fluorescent background is formed if Pd(II) is present. On exposure to ammonia atmosphere, the orange spot turns intense red or red-orange. Limit of idn.: 2 µ. Limit of diln.: 1:25,000. This test when conducted in a micro test tube, NaOH soln. is used in place of ammonia, an intense red, purple or red-brown colour, characteristic of Pd(II) develops. Only Hg(II) gives a more or less similar test. Addition of EDTA removes interference by Hg(II). The other interference-causing species are: Hg(I), As(III), Au(III), I⁻, NO₃⁻, N₃⁻, SO₃²⁻, C₂O₄²⁻, and thiourea. In the test for Pd(II) using EDTA, acriflavine, and NaOH soln., a deep bright-red or red-orange ppt. is formed; this test is also characteristic of Pd(II). NH₄⁺, PO₄³⁻, As(III), I⁻, NO₃⁻, SCN⁻, VO₃⁻, SO₃²⁻, Au(III),[Fe(CN)₆]⁴⁻, and[Fe(CN)₅]NO₃²⁻ interfere. A large number of other ions do not interfere. The nature of the coloured products formed in the various tests are discussed.

INTRODUCTION

Various micro- and spot-test procedures are available in literature⁵, ⁹, ¹⁷-²⁰ for the detection of palladium(II). In the present communication, a new, simple and sensitive spot test for palladium(II) is described using the common antiseptic dye acriflavine (3,5-diamino-10-methylacridinium chloride monohydrochloride) (I) as the reagent.

Acriflavine was earlier used for the detection of carboxylic acid group in organic compounds, nitrite, bromide, and bromate ion. The present test for
palladium involves the reaction of an aqueous acriflavine solution with an acidic solution of Pd(II) ion when a deep orange precipitate is formed. On adding ammonia solution the colour of the precipitate changes to deep red with its simultaneous dissolution giving a deep red solution. However, if sodium hydroxide is added in place of ammonia, the orange precipitate assumes an intense purple or purple-brown colouration, but is not dissolved. The results of the reaction (with ammonia) are more satisfactorily and interestingly observed on the filter paper. On the other hand, the reaction with sodium hydroxide is best observed in a micro test tube.

\[
\text{HC1} \cdot \text{H}_2\text{N} \quad \text{NH}_2
\]

In another test, the palladium(II) solution forms a pale yellow soluble complex with EDTA, which on treatment with acriflavine and sodium hydroxide solutions forms an intense scarlet red or deep red precipitate. Sometimes it is deep red-orange.

**Experimental**

Reagents

*Acriflavine solution.* A 0.1 percent w/v solution in water, prepared from B. P. C. grade reagent.

*Palladium(II) solution.* A 0.5 percent w/v solution in water acidified with sufficient hydrochloric acid.

*Concentrated ammonia.* Sp gr. 0.8 or 0.9.

*Sodium hydroxide solution.* 5 percent w/v solution in water.

Procedures

**On filter paper.** Place a drop of 0.1 percent aqueous acriflavine solution on a good quality ordinary filter paper (not quantitative paper) and mix with it 1 drop of slightly...
Palladium(II) Chloride Reaction with Acriflavine

acidic test solution. Let the mixed drop spread on the paper by capillary action, which may take 1 min. A more or less deep orange-coloured spot or ring surrounded by fluorescent yellow background (of the dye) appears if palladium is present. Now bring the spotted part of the paper over the mouth of ammonia bottle. The orange spot turns deep red or intense red-orange.

Limit of detection : 2 µg Pd(II)

Limit of dilution : 1 : 25,000.

In a micro test tube. To 5 drops (0.25 ml) of the slightly acidic test solution add 1 or 2 drops of acriflavine solution. A positive response is indicated by the formation of an orange precipitate or turbidity depending on the quantity of palladium present. Upon the addition of a drop of 5 percent sodium hydroxide solution, the orange compound changes to intense red, purple, or red-brown.

Limit of detection : 10 µg Pd(II)

Limit of dilution : 1 : 25,000.

Acriflavine/EDTA test for palladium(II). Take 5 drops (0.25 ml) of the slightly acidic test solution in a micro test tube, and add successively 5 drops of 3 percent w/v solution of disodium salt of EDTA (in water) and 5 drops of 0.1 percent aqueous acriflavine solution. The resulting deep yellow solution (due to the dye) is then alkaliified with 5 drops of 5 percent sodium hydroxide solution. Allow the tube to stand without shaking its contents. A more or less intense red or red-orange precipitate is formed immediately or within a few sec. if palladium is present.

Limit of detection : 15 µg Pd(II)/0.25 ml.

RESULTS AND DISCUSSION

Interferences

The following ions do not interfere in the tests for palladium involving acriflavine and ammonia on the filter paper or acriflavine and sodium hydroxide in micro test tube: Tl(II), NH₄⁺, Ag⁺, Zn(II), Cd(II), Sn(II), Cu(II), Ni(II), Co(II), Mn(II), Ca(II), Sr(II), Ba(II), Mg(II), Fe(II), Fe(III), As(III), Sb(III), Bi(III), In(III), Sn(II), Ru(III), La(III), Eu(III), Al(III), Cr(III), Pt(IV), Th(IV), Zr(IV), Ce(IV), NO₃⁻, VO₄⁻, IO⁻, IO₃⁻, BrO₃⁻, F⁻, Cl⁻, Br⁻, HCOO⁻, CH₃COO⁻, SO₄²⁻, CrO₄²⁻, Cr₂O₇²⁻, MoO₄²⁻, WO₄²⁻, S₂O₃²⁻, SiO₃²⁻, [Fe(CN)₆NO]²⁻, [Fe(CN)₆]³⁻, [Fe(CN)₆]⁴⁻, and salicylate. Hydrogen peroxide and formaldehyde also do not interfere.
The following ionic and other species constitute interferences in these tests:

Hg(I), Hg(II), Au(III), I\(^{-}\), NO\(_2\)\(^{-}\), N\(_3\)\(^{-}\), MnO\(_4\)\(^{-}\), SO\(_4\)\(^{2-}\), C\(_2\)O\(_4\)\(^{2-}\), pyridine \(\alpha\), \(\alpha'\)-dipyridyl, hydrazine sulphate, and dimethyl-glyoxime. Whereas EDTA completely inhibits the test on filter paper, its presence gives an entirely different coloured but specific product in the test in micro test-tube. PO\(_4\)\(^{3-}\) interferes in the 'filter paper' test, but very slight interference is caused in 'micro test tube' test.

The following relevant points should be followed to overcome some of the interferences described above: (i) MnO\(_4\)\(^{-}\) may be removed by boiling the test solution with a few drops of conc. hydrochloric acid until permanganate colouration is destroyed. (ii) NO\(_2\)\(^{-}\) may be removed by heating the solution with a few crystals of sodium azide and a drop of conc. hydrochloric acid. (iii) In presence of I\(^{-}\), palladium(II) forms a dark brown-black anionic species \([\text{PdI}_4]^{2-}\) which can be destroyed by heating with a few crystals of ammonium persulphate and a drop of conc. sulphuric acid; by this treatment all iodide content is oxidized to free iodine which is expelled in the form of violet vapours; the solution is then filtered, and the test performed with the filtrate. (iv) In presence of Hg(I), the test solution should be shaken thoroughly with a few crystals of ammonium persulphate, filtering off the solution, and performing the test with filtrate. (v) In presence of BrO\(_3\)\(^{-}\), IO\(_3\)\(^{-}\) and IO\(_4\)\(^{-}\) to get a positive response, the test solution should be made as feebly acidic as possible. In sufficiently acidic solutions, IO\(_3\)\(^{-}\) and IO\(_4\)\(^{-}\) cause a negative reaction; the BrO\(_3\)\(^{-}\) on the other hand, is likely to be decomposed at low pH, thus releasing free bromine which reacts with acriflavine giving an orange-brown precipitate.

In the acriflavine/EDTA test, most cations and anions do not interfere. Only following ionic species interfere: NO\(_2\)\(^{-}\), I\(^{-}\), NH\(_4\)\(^{+}\), C\(_3\)O\(_4\)\(^{2-}\), SCN\(^{-}\), VO\(_3\)\(^{-}\), SO\(_3\)\(^{2-}\), PO\(_4\)\(^{3-}\), As(III), [FeCN\(_6\)]\(^{3-}\), [Fe(CN)_3NO]\(^{2-}\); Thiourea also interferes. In presence of Hg(I) and/or a halogen, the test solution after treatment with EDTA should be filtered, and further procedure adopted on the filtrate. In presence of BrO\(_3\)\(^{-}\), the test solution should be as feebly acidic as possible.

Palladium(II) solution in presence of iodine, periodate, or ferrocyanide (not ferricyanide) when treated with acriflavine solution followed by alkaliification with sodium hydroxide, produces an unusually bright and deep red colouration. This test is positive even in the presence of Au(III), As(III) and PO\(_4\)\(^{3-}\); however the ultimate product may be deep red-orange precipitate instead of deep red colouration.

**Nature of the product in palladium test with acriflavine:**

Acriflavine, \([\text{C}_{14}\text{H}_{15}\text{N}_3\text{Cl}]^+\text{Cl}^-\) when treated in aqueous solutions with complex ions, reveals its tendency to get precipitated in the form of salts. These salts are formed
by the replacement of chloride ion attached to the heterocyclic nitrogen. Thus, such salts as acriflavine chromate, \((C_{14}H_{15}N_3Cl)_2CrO_4\), acriflavine antimony tartrate etc. are described in literature. It has also been observed that acriflavine is also precipitated out from its aqueous solution when treated with such complex ions as ferricyanide, ferrocyanide, nitroprusside, dichromate, thiocyanate, and vanadate etc. In all these cases, the formation of corresponding salts of acriflavine are expected. Certain allied-natured salts, viz., those of acridine, 3,6-diamino-10-iodomethylacridine are also known. Similarly, when anhydrous palladium chloride \((PdCl_2)\) is dissolved in water containing sufficient hydrochloric acid, there is formed a dark red-brown solution which seems to contain unstable chloropalladatoic acid \(H_2[PdCl_4]\), the latter yielding tetrachloropalladate ions \((PdCl_4)^{2-}\) in solution. In the course of present investigation, it was thought that the orange product (precipitate) formed by the interaction of palladium(II) solution and acriflavine, probably involved the reaction of \((PdCl_4)^{2-}\) anion with the dye cation \((C_{14}H_{15}N_3Cl)^+\), resulting in the formation of the corresponding salt 'acriflavine tetrachloropalladate', i.e., \((C_{14}H_{15}N_3Cl)_2(PdCl_4)\). The analytical, magnetic, infrared and electronic spectral data, however, have ruled out the formation of such type of salt. These findings have given a strong indication to the formation of a 1:1 (metal:ligand) chlorine-bridged complex having the structure \(\Pi\) in which the metal is linked to one of the primary amino groups of the dye through nitrogen. The \(\Pi\) is practically insoluble or very feebly soluble in cold water and organic solvents, but considerably (though not completely) soluble in hot or boiling water, giving a yellow solution with intense green fluorescence. The elemental analysis of the complex gave following results: Found: C, 32.8; H, 4.4; N, 8.3; Pd, 21.4. Req'd for \([C_{14}H_{15}N_3Cl]^+Cl^- PdCl_2 2H_2O\): C, 33.0; H, 3.7; N, 8.2; Pd, 20.8.

The i.r. study of the complex points to a direct co-ordination of palladium with the amino group of acriflavine. The presence of a new band below 300 cm\(^{-1}\) at the same time indicates bridging Pd-Cl grouping i.e. \((Pd-Cl-Pd)\). The observed changes in the band positions of the i.r. spectrum of acriflavine Pd(II)Cl\(_2\) complexes as compared to that of pure acriflavine are shown in Table I.
Table I

ASSIGNMENTS AND SHIFTS OF THE INFRARED BANDS
IN ACRIFLAVINE AND ACRIFLAVINE-PdCl₂ COMPLEX

<table>
<thead>
<tr>
<th>Band positions</th>
<th>Acriflavine</th>
<th>Acriflavine/PdCl₂ complex</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3590 cm⁻¹</td>
<td>( \nu (\text{O-H}) ) water of hydration</td>
</tr>
<tr>
<td>3340 cm⁻¹</td>
<td>3380</td>
<td></td>
<td>( \nu \text{ asym} \text(NH}_2)</td>
</tr>
<tr>
<td>3220 cm⁻¹ ₜ</td>
<td>3250 cm⁻¹</td>
<td></td>
<td>( \nu \text{ sym} \text(NH}_2)</td>
</tr>
<tr>
<td>1660 cm⁻¹</td>
<td>1610 cm⁻¹</td>
<td></td>
<td>( \delta \text(NH}_2); A negative shift indicates further involvement of (-\text{NH}_2) group in bonding.</td>
</tr>
</tbody>
</table>

470 cm⁻¹      \( \nu (\text{Pd-N}) \).

290 cm⁻¹      Bridging Pd-Cl stretching vibration, i.e., \( \nu (\text{Pd-Cl-Pd}) \).\(^{14, 15}\)

The terminal metal-Cl bands appear generally above 300 per cm. The bridging Pd-Cl bands indicate that the complex is at least dimeric.

Electronic Spectrum

In square-planar complexes, one should expect the following spin allowed transitions: (i) \( ^1\text{A}_g \rightarrow ^1\text{A}_{2g} \), (ii) \( ^1\text{A}_g \rightarrow ^1\text{B}_{1g} \), and (iii) \( ^1\text{A}_g \rightarrow ^1\text{E}_g \). Since the spectra of square-planar Pd(II) complexes show strong absorption in the range of 200 m\( \mu \) - 750 m\( \mu \).
It is very difficult to find bands corresponding to these transitions. However, a single band at 18,518 cm\(^{-1}\) (540 m\(\mu\)) observed in the case of acriflavine/PdCl\(_2\) complex is assigned to \(^1A_2g\rightarrow^1B_{1g}\), a transition which usually absorbs in this region.\(^{18}\) A second band observed at 14,705 cm\(^{-1}\) (680 m\(\mu\)) may be due to d–d transition\(^{19}\). On the basis of preceding discussion, therefore, the following structure (II) is proposed for the acriflavine/PdCl\(_2\) complex. In this dimeric, halogen (chloro)-bridged structure, palladium is tetra-coordinate, thus having square-planar arrangement of the ligands around it.

\[ \text{Cl}^- \quad \text{H}_3\text{N}^+ \quad \text{H}_2 \quad \text{Cl}^- \quad \text{H}_2\text{O} \quad \text{Pd} \quad \text{N} \quad \text{Cl}^- \quad \text{H}_3\text{C} \quad \text{Cl}^- \quad \text{H}_2\text{O} \]

The structure II is further supported by the following experimental evidences:

(i) It is practically insoluble or very slightly soluble in cold water and organic solvents, but considerably (though not completely) soluble in hot or boiling water, giving a yellow solution with intense green fluorescence. With AgNO\(_3\) and \(\text{Hg}_2(\text{NO}_3)_2\), this solution gives a positive test for Cl\(^-\) ions. This shows that the chloride ion attached to the heterocyclic nitrogen is intact after complex formation. (ii) The solution of II in hot water is fluorescent yellow (like solution of the free dye) which gives a violet colour with nitrite + acid, a characteristic reaction of acriflavine due to its amino groups. This shows that in II, at least one of the two amino groups of I is free to undergo diazo reaction. Therefore, the only possibility that remains for the attachment of the inorganic moiety (PdCl\(_2\)) to the dye molecule is through the other amino group, as in structure II. The presence of two water of hydration molecules is revealed by the corresponding loss in weight on heating around 200°C.

The red purple product formed by the action of ammonia or NaOH on II possibly involves dehydrohalogenation at the 8-amino-hydrochloride groups. The resulting red purple dehydrohalogenated compound reverts to the original compound (II) on acidification.

The nature of red-coloured products formed by the action of ammonia or sodium hydroxide on II is not well understood as yet. These may be ammine or hydroxo complexes of II.
Nature of the product in acriflavine/EDTA test for palladium(II):

EDTA (\(-\text{H}_2\text{Y}\)) on reaction with an acidic palladium chloride solution gives a pale yellow or nearly colourless Pd(II)-EDTA complex,\(^7\), \(^8\) \(\text{PdH}_2\text{YCl}_2\); and how the latter reacts with acriflavine on being alkalized with sodium hydroxide, giving a deep red or red-orange product, is yet to be worked out.

References

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STRUCTURES OF "SILVER BISMUTH IODIDE" AND "THALLIUM BISMUTH IODIDE"

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BISMUTH (III) halides are known to have a tendency to combine with one or more molecules of halides of other elements to form double halides \(^1\)-\(^5\). Thus, in 1922, Cannieri and Perina\(^1\) described the formation of a beautifully coloured double iodide of thallium(I) and bismuth(III). Upon the addition of KI to an acid solution containing both Tl and Bi ions, "thallium bismuth iodide" or "bismuth thallium iodide" (\(\text{Ti}_2\text{BiI}_5\) or \(2\text{TI.BiI}_3\)) separates out as an insoluble wine-red, microcrystalline precipitate. This reaction was originally used as a means for the determination of bismuth\(^4\), and later, for the detection of TI(I), Bi(III) and I\(^–\) ions\(^6\). Like the formation of thallium bismuth iodide, a deep maroon-red or brownish-maroon precipitate of "silver bismuth iodide" or "bismuth silver iodide" (\(\text{Ag}_2\text{BiI}_5\) or \(2\text{AgI.BiI}_3\)) is formed when a silver(I) ion solution is treated with the yellow solution of potassium iodobismuthate, \(\text{KBiI}_4\), or its acid, iodobismuthic acid, \(\text{HBiI}_4\)\(^7\). This reaction has been used for the spot test detection of silver(I)\(^7\).

\[
\text{KI} \quad \text{Bi}^{2+} + 3\text{I}^- \rightarrow \text{BiI}_3 \rightarrow \text{KBiI}_4 \rightarrow \text{MBiI}_4 \rightarrow \text{M}_2\text{BiI}_5
\]

The formation of silver bismuth iodide and thallium bismuth iodide possibly involve the following series of reactions to form a product of general formula \(\text{M}_2\text{BiI}_5\):

Since the structures of metal-bismuth double iodides (\(\text{M}_2\text{BiI}_5\)) have not been worked out as yet by any worker, as is apparent from the literature, we have endeavoured to solve the problem. With the help of elemental analysis and infrared studies we have been able to evolve the structures of \(\text{Ag}_2\text{BiI}_5\) and \(\text{TI}_2\text{BiI}_5\).

The I. R. spectra of \(\text{Ag}_2\text{BiI}_5\) and \(\text{TI}_2\text{BiI}_5\) were recorded on an extended range, with slow speed, so as to get a detailed picture, especially of the cesium bromide region (700-250 cm\(^{-1}\)).

For \(\text{Ag}_2\text{BiI}_5\) (Found: Ag, 19.7; Bi, 19.1; \(\text{req'd: Ag, 20.3; Bi, 19.7\%}\)), the I.R. bands were observed at 650 cm\(^{-1}\), 530 cm\(^{-1}\), 435 cm\(^{-1}\) and 410 cm\(^{-1}\); these bands are assigned to metal-iodide ring vibration. Other bands observed above 300 cm\(^{-1}\), \(\text{viz. at 385 cm}^{-1},\ 370\ \text{cm}^{-1},\ 345\ \text{cm}^{-1}\), and 325 cm\(^{-1}\) are assign-
ed to “terminal metal-iodide” stretching vibration, \( v(\text{Bi-I}) \). The bands observed below 300 cm\(^{-1}\), \( v(\text{Bi-I}) \), 280 cm\(^{-1}\) and 265 cm\(^{-1}\), are assigned to “bridged metal-iodide” stretching vibration, \( v(\text{Ag-I-Ag}) \) and/or \( v(\text{Bi-I-Ag}) \).

The dried compound \( \text{Ag}_2\text{BiI}_5 \) is practically insoluble in water, and gives no iodide ions in solution when stirred with it. This indicates a non-ionic, polymeric or ring type structure\(^a\)(I) for \( \text{Ag}_2\text{BiI}_5 \). When treated with pyridine, the dark maroon \( \text{Ag}_2\text{BiI}_5 \) turns deep mustard yellow, which is an indicative of pyridine coordination, possibly having the structure II.

\( \text{Tl}_2\text{BiI}_5 \) (Found: Tl, 31.8; Bi, 16.2; Req. d: Tl, 32.5; Bi, 16.6%) upon treatment with sodium thiosulphate loses its red-orange colour, and yellow-coloured thallous iodide(TII) is left behind. The I. R. spectrum of \( \text{Tl}_2\text{BiI}_5 \) showed bands nearly at the same positions as found in the case of \( \text{Ag}_2\text{BiI}_5 \). Thus, an analogous ring structure (II) is also assigned to this compound.

REFERENCES

2. G. CANNERI, ibid, 52, 37 (1922).
Abstract of the paper entitled 'Studies of the Irreversible Reduction of Oxygen at the Dropping Mercury Electrode'.


The nature of reduction process of Oxygen at the Dropping Mercury Electrode has been investigated polarographically. It is found that Current at the foot of the curves is independent of \( h^{3/2} \) while it showed dependence on \( h^{3/2} \) when current approached \( i_d \). Also \( i_d \) is linearly variant with \( h^{3/2} \) showing that the polarographic reduction of Oxygen is irreversible in nature.

\[
\frac{i_d}{cm^{2/3} \cdot t^{1/6}} \text{ plotted against } \frac{t^{1/6}}{m^{3/6}}
\]

The linear increase of

\[
\frac{i_d}{cm^{2/3} \cdot t^{1/6}}
\]

demonstrated the failure of IIKOVIC's equation. The value of \( E^{3/2} \) tends to become more negative with decrease in drop time. These observations add in proof of the irreversible reduction of Oxygen at d.m.e. ........................