

Spectrophotometric Determination of Platinum(II) using Hexachloroiridate(IV)

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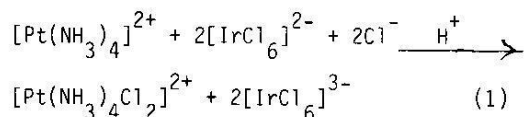
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Introduction

For our radiation chemical and photochemical studies of some Pt(II) and Pt(IV) amine complexes in aqueous solution, we were interested in the stable final product analysis. This type of analysis of the irradiated solutions can lead to important mechanistic conclusions. Irradiation of platinum complexes may lead to redox reactions resulting in stable products having a different oxidation state of the metal ion. For example, irradiation of Pt(II) complexes may lead to the formation of Pt(IV) and Pt(O) species [1-5]. In pulse-irradiated or flash-photolyzed solutions, analysis of the products becomes difficult because very small concentrations (in micromolar range) are involved. Therefore an analytical method was needed to detect change in the concentration of Pt(II) (and Pt(IV)) to a few micromolar level.

Several methods have been reported for determination of trace amounts of platinum(II), such as stannous chloride, p-nitrosodimethylaniline or iodide methods [6]. Our preliminary experiments were based on the oxidation of ferrocyanide to ferricyanide by Pt(IV) in deaerated aqueous solution, measured by an increase in the ferricyanide absorption at 420 nm. Any decrease in Pt(II) concentration is equivalent to the corresponding increase in Pt(IV) (or Pt(O)) concentration. This method worked well; however it was sensitive to light and to the presence of oxygen in the solution.

Here in this paper we describe a new spectrophotometric method for determining the change in Pt(II) concentration. This method is convenient and yields more reliable results. The method is based on the oxidation of Pt(II) to Pt(IV) by $K_2[IrCl_6]$ in solution containing excess amounts of H^+ and Cl^- ions [7]. For tetraammineplatinum(II) complex, used in our study, the reaction can be represented as follows:



This equation shows that for every molecule of Pt(II) oxidized, two molecules of $[IrCl_6]^{2-}$ are consumed. This reaction goes to completion readily and can be used for quantitative determination of Pt(II) ions. Since $[IrCl_6]^{2-}$ exhibits strong absorption peak at 487 nm, whereas the other species present do not absorb significantly at this wavelength, a spectrophotometric determination is possible.

Experimental

$K_2[IrCl_6]$ and $[Pt(NH_3)_4]Cl_2$ were supplied by Platinum Chemicals. All other chemicals were of reagent

grade. Distilled water purified by Millipore Super-Q system was used. UV-VIS absorption spectra were recorded on a Cary 118C spectrophotometer with 1 cm cell. All experiments were carried out at $25 (\pm 0.5) ^\circ\text{C}$.

Stock solution of $[\text{IrCl}_6]^{2-}$ was prepared by dissolving 0.266 g of $\text{K}_2[\text{IrCl}_6]$ in one litre of solution which was 0.2 M in both HCl and NaCl, giving $550 \mu\text{M}$ solution. For analyses, 5 ml of $[\text{IrCl}_6]^{2-}$ stock solution was added to an equal volume of test solution. The spectrum of the solution was recorded after mixing and thermostating the solution for about half an hour.

Results and Discussion

A calibration curve was drawn using varying amounts of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in the test solution ($0.250 \mu\text{M}$) added to an equal volume of $550 \mu\text{M}$ $[\text{IrCl}_6]^{2-}$ solution and noting the absorption of resulting solution at 487 nm. The results showed that decrease in the absorption at 487 nm was linear with Pt(II) concentration and the stoichiometric ratio was 2 $[\text{IrCl}_6]^{2-}$ per 1 Pt(II), as suggested by equation (1). The calibration curve showing absorption of solution versus concentration of Pt(II) is shown in Figure 1. The least square regression analysis showed a slope of $4020 \pm 40 \text{ M}^{-1}$ which for 1 cm cell is the same as the molar absorption coefficient of $[\text{IrCl}_6]^{2-}$ (in $\text{M}^{-1} \text{cm}^{-1}$) at 487 nm. This absorption coefficient is the same, within experimental error, as reported by Chang and Garner [8] ($4050 \pm 35 \text{ M}^{-1} \text{cm}^{-1}$).

Effect of pH and presence of various reagents in the solution on analysis

of Pt(II) was checked. The reagents selected for this purpose were those normally present or could be formed while carrying out radiolysis or photolysis experiments on Pt(II) and Pt(IV) solutions. It was found that the results are independent of initial pH of the test solution in 5.0 to 10.0 range. Furthermore the analysis was not effected by presence of acetone (0.4 M), tert-butyl alcohol (0.2 M) and isopropyl alcohol (2.0 M). The presence of Pt(IV) compounds in the solution does not interfere with the Pt(II) determinations. This was checked for $\text{trans}-[\text{Pt}(\text{NH}_3)_4(\text{OH}_2)]^{2+}$ (50-100 M) and $\text{trans}-[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ (40-60 μM). In addition, oxidizing agent H_2O_2 (50-400 μM) and reducing agent N_2H_4 (50-200 μM) when present in the solution do not effect Pt(II) analysis. However, when hydrazine was present in a test solution containing 60 μM of Pt(IV), it gave a positive test for Pt(II). This can be explained due to the reduction of Pt(IV) compounds to Pt(II) by hydrazine. The technique worked satisfactorily with other Pt(II)

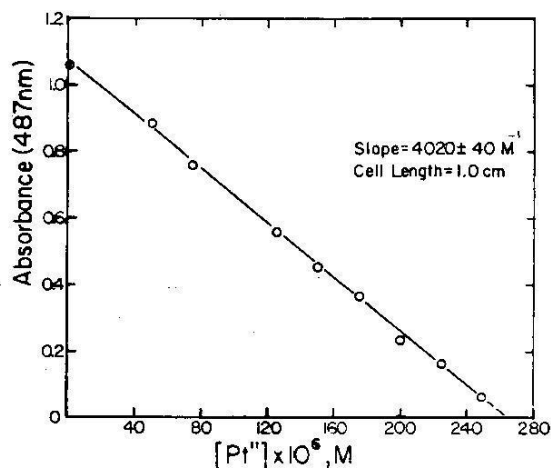


Fig.1: Calibration curve for $[\text{IrCl}_6]^{2-}$ - Pt(II) reaction.

Absorption of IrCl_6^{2-} solution at 487 nm versus concentration of platinum (II)

compounds such as $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O}_2)]^{2+}$ indicating that other Pt(II) complex ions are also quantitatively oxidized by $[\text{IrCl}_6]^{2-}$. The presence of lower oxidation states of platinum in form of suspended metallic platinum, which was formed by radiolysis in some experiments, does not appear to interfere with the Pt(II) analysis under the experimental conditions employed since removal of the metallic platinum by filtration does not alter the results.

The above results and those reported by others [4,7] for related Pt(II) complexes suggest that the results obtained by foregoing procedure provide a valid measure of the total concentration of Pt(II) in the solution. This method was preferred over the other methods since it is a rapid method, does not require prior deaeration, and light conditions are also less stringent. The stock solution of $\text{K}_2[\text{IrCl}_6]$, 0.2 M in HCl and NaCl, when stored away from direct light is stable for several days. When mixed with the Pt(II) test solution, the reaction takes place readily and the absorption of the resulting solution at 487 nm remains unchanged for at least 12 hours. Because of very high absorption coefficient of $[\text{IrCl}_6]^{2-}$ at 487 nm ($4020 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}$), very small concentration of Pt(II) in the solution (of order of 1 μM) can be determined using 1 cm spectrophoto-

meter cell. For determining still lower concentrations of Pt(II), a cell with longer optical path length can be used.

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References

1. D.K.Storer, W.L.Waltz, J.C.Brodovitch and R.E.Eager, *Int.J.Radiat.Phys.Chem.*, **7**, 693, (1975)
2. J.C.Brodovitch, D.K.Storer, W.L.Waltz and R.E.Eager, *Int.J.Radiat.Phys.Chem.*, **8**, 467, (1976)
3. A.Vogler, A.Kern and J.Huttermann, *Agnew.Chem.Int.Ed.Engl.*, **17**, 524, (1978)
4. A.V.Loginov, V.A.Yakovler and G.A.Shagisultanova, *Koord.Khim.*, **5**, 733, (1979)
5. H.M.Khan, W.L.Waltz, R.J.Woods and J.Lilie, *Can.J.Chem.*, **59**, 3319, (1981)
6. E.B.Sandell, "Colorometric Determination of Traces of Metals", Third Ed., Interscience, New York, p.726, (1959)
7. J.Halpern and M.Pribanic, *J.Am.Chem.Soc.*, **90**, 5942, (1968)
8. J.C.Chang and C.S.Garner, *Inorg.Chem.*, **4**, 209, (1965)