[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

THE QUANTITATIVE DETERMINATION OF PALLADIUM BY MEANS OF 6-NITROQUINOLINE

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The use of certain organic complexes in the formation of stable coördinated salts with metals of the platinum group is well known. Those of the oximes, aromatic nitroso-amines and hydroxyquinolines are of great value in the quantitative removal of these metals from solution. This is particularly true with platinum and palladium.[2]

Bargallini and Bellinois[3] state that in the case of the hydroxyquinolines, the condition ≡C—O—M—N= (where M is one metallic equivalent and in which the ring is closed by a secondary valence) must be *met. Thus the metal replaces the hydrogen of the hydroxyl (which must* be in the eighth position) and is connected with the N of the quinoline molecule.

One of us[4] found that other substituted quinolines would also act with the formation of coördinated salts with palladium. The best of these is 6-nitroquinoline. The metallic grouping formed in this case is not with the nitrogen of the quinoline structure, but with the nitrogen of the nitro group. The structural condition here is ≡C—N<O>M<O>N—C≡,[5] in which the metal, palladium, exhibits a coördination number of four. This compound has been found to be so stable and so insoluble in aqueous solutions that it may be used as a means of quantitatively removing palladium. As it has no precipitating effect on solutions of ruthenium, rhodium, *osmium, iridium and platinum, it may also be used in separating palladium* from the entire platinum metal group.

Experimental Part

Preparation of Palladium Chloride Solution.—To insure the purity of the palladium chloride used, a few grams of the dry C. P. salt as purchased from a leading supply house was dissolved in hot water acidulated with hydrochloric acid. The metal was precipitated from this solution by the addition of previously tested pure zinc dust. The spongy metal

[1] This paper is based upon a thesis submitted by A. H. Riesmeyer to the Faculty of Bucknell University in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Ogburn, THIS JOURNAL, **48**, 2507 (1926).

[3] Bargallini and Bellucci, *Gazz. chim. ital.*, **53**, 605 (1923).

[4] Ogburn, THIS JOURNAL, **48**, 2493 (1926).

[5] This grouping is in accord with Lowry's (*J. Soc. Chem. Ind.*, **42**, 462 (1923)) interpretation of the structural formula for the precipitate of nickel with dimethylglyoxime, except that in this case nickel has a coördination number of six.

was washed free from chlorides and dissolved in freshly prepared *aqua regia* (1:3). After evaporating this solution to dryness and extracting with hydrochloric acid, several repeated evaporations with the latter reagent were carried out in order to expel all nitrogen oxides. The dihydrate, $PdCl_2 \cdot 2H_2O$, thus obtained was dissolved in a small quantity of distilled water and the palladium precipitated as $Pd(C_4H_7O_2N_2)_2$ by means of a 1% alcoholic solution of dimethylglyoxime *in the cold*.[6] After stirring, this bright yellow precipitate was filtered, washed with a small quantity of cold water containing a few cubic centimeters of alcohol and dried in an electric oven at 105°. It was then carefully ignited in air, heated for twenty minutes at red heat in a stream of hydrogen, cooled and the metallic palladium thus obtained weighed. A definite quantity (4.780 g.) of this metal was subsequently dissolved in *aqua regia* and the solution evaporated to dryness. The residue was taken up with hydrochloric acid; this was followed by several evaporations with the latter reagent to remove all nitrogen oxides, and the solution diluted to one liter. The resulting palladium chloride solution, which was only slightly acid, was analyzed for its metal content per cubic centimeter by treating a known portion with zinc dust until all color was removed from the solution. (The colorless solution gave no precipitate with dimethylglyoxime, hydrogen sulfide, mercuric cyanide or 6-nitroquinoline—thus the absence of palladium was assured.) Excess zinc was dissolved in dilute hydrochloric acid and the spongy palladium was filtered, washed free from chlorides, dried, heated at red heat in a stream of hydrogen, cooled and then weighed. Results of two such determinations were

Weight of boat plus metal, g.	3.2723	3.2724
Weight of boat, g.	3.2484	3.2485
Weight of metal, g.	0.0239	0.0239
Amount of solution used, cc.	5.0	5.0
Weight of metallic Pd per cc., g.	0.00478	0.00478

This solution was used in the following work.

Preparation of 6-Nitroquinoline Solution.—In the analytical determinations recorded below, a hot saturated aqueous solution of this reagent was used.

The Removal of Palladium from a Solution of Palladium Chloride.—A measured amount of palladium chloride solution was heated to boiling and treated with a hot saturated solution of 6-nitroquinoline. After stirring, the mixture was allowed to boil for about five minutes. More of the reagent was then added until no further precipitation was observed. After standing for fifteen to twenty minutes, the thick, flocculent yellow precipitate was filtered. (A small portion of the filtrate was treated with

[6] To prevent any platinum from being precipitated.

more reagent to assure the complete precipitation of the palladium.) The precipitate was washed with distilled water until free from chlorides (as ascertained by the silver nitrate test), dried, ignited carefully in air, then heated for thirty minutes at a red heat in a stream of hydrogen, cooled[7] and the metallic palladium weighed. The results were as follows:

Weight of boat plus metal, g.	8.0769	5.9559	6.8619
Weight of boat, g.	8.0531	5.9322	6.8524
Weight of metallic Pd, g.	0.0238	0.0237	0.0095
Amount of $PdCl_2$ solution used, cc.	5.0	5.0	2.0
Weight of metal per cc., g.	0.00476	0.00474	0.00475
Weight of metal per cc. (theoretical)	0.00478	0.00478	0.00478

These results show conclusively the accuracy which is attained by the use of 6-nitroquinoline as a reagent for the removal of palladium from solutions of its salts in which there is present only a small amount of the metal.

The Removal of Palladium from a Solution of All the Platinum Metals.—Solution number 1 below was made to contain 95% by weight of palladium and 1% of each of the other platinum metals, that is, ruthenium, rhodium, osmium, iridium and platinum. The solutions of each of these used were those of the chlorides of the metals which were prepared in this Laboratory directly from the pure metal, except in the case of the osmium, which was prepared from pure crystalline OsO_4. Solution number 2 below was made to contain equal quantities of each of the six metals. The procedure of analysis was followed as shown above. The results obtained were as follows:

	Solution No. 1		Solution No. 2	
Weight of boat and metal, g.	3.2686	3.1350	3.6574	3.3210
Weight of boat, g.	3.2476	3.1262	3.6359	3.3123
Weight of metallic Pd, g.	0.0210	0.0088	0.0215	0.0087
Amount of $PdCl_2$ solution used, cc.	5.0	2.0	5.0	2.0
Weight of metal per cc. (recovered), g.	0.00420	0.00440	0.0043	0.00435
Weight of metal per cc. (theoretical), g.	0.00478	0.00478	0.00478	0.00478

These determinations, while showing a slight influence of the other metals of the platinum group on the removal of palladium from such a mixture by means of 6-nitroquinoline, are sufficiently close to indicate its usefulness as a quantitative procedure. With larger quantities of metals present it could, in all probability, be made more accurate.

The Separation of Palladium from Platinum.—As platinum is the most common metal of this group which is prevalent with palladium both in nature and in commerce, it would seem important to know whether large amounts of this particular metal would influence this separation. Also, it is with platinum, especially, that most of the organic coördinated salts are formed.

[7] Cooling the spongy metal in carbon dioxide is preferable to cooling in hydrogen.

Solution number 1 below was made to contain 20% of palladium and 80% of platinum, while solution number 2 was made to contain 80% of palladium and 20% of platinum. Following the above procedure, the results were

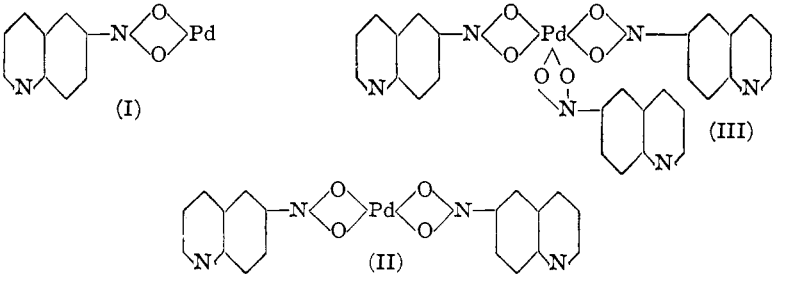
	Solution No. 1		Solution No. 2	
Weight of boat and metal, g.	3.1352	3.2534	3.3326	3.5449
Weight of boat, g.	3.1260	3.2487	3.3096	3.5359
Weight of metallic Pd, g.	0.0092	0.0047	0.0230	0.0090
Amount of $PdCl_2$ solution used, cc.	2.0	1.0	5.0	2.0
Weight of metal per cc. (recovered), g.	0.0046	0.0047	0.0046	0.0045
Weight of metal per cc. (theoretical), g.	0.00478	0.00478	0.00478	0.00478

These determinations show that platinum does not interfere with the quantitative removal of palladium by this reagent.

The Determination of the Empirical Formula of the Palladium Compound.—With such organic substances, palladium forms either an additive (double) salt or a coördinated (inner) one. If the precipitated compound formed in the above determinations should contain chlorine, it would indicate an additive compound. If no chlorine were found, the indications would point strongly toward a coördinated one.

Sufficient fuming nitric acid was added to a small quantity of the compound, *which had been washed free from chlorides* from the precipitating mixture, to insure its solution.[8] Excess nitrogen oxide was removed by boiling. When the solution had attained a clear straw yellow color, it was diluted and a portion taken and treated with silver nitrate. No trace of silver chloride precipitate was observed. This process was repeated on several samples of the compound with the same result.

Three possible structural formulas were then considered. These represented the palladium with coördination numbers of two, four and six, and were as follows: $Pd{\cdot}C_9H_6NNO_2$ (1), $Pd{\cdot}(C_9H_6NNO_2)_2$ (2) and $Pd{\cdot}(C_9H_6NNO_2)_3$ (3).



The molecular weights of these compounds are as follows: (1) 280.813, (2) 454.926 and (3) 629.039. Their percentage composition with respect to palladium, carbon and hydrogen is

[8] Concentrated hydrochloric acid has no effect on the compound.

	(1)	(2)	(3)
Palladium, %	37.99	23.45	16.96
Carbon, %	38.47	47.50	51.53
Hydrogen, %	2.16	2.66	2.88

An analysis of the yellow compound was then made which included determinations for palladium, carbon and hydrogen.

The palladium content was obtained by the reduction of the compound at red heat in a stream of hydrogen, after it had been previously washed, dried and ignited carefully in air. After cooling the spongy metal was weighed.

The carbon and hydrogen were determined by the usual combustion method,[9] in which the complete oxidation of the organic compound was attained with the formation of carbon dioxide and water, which were collected separately and weighed.

Six such determinations were made. A typical pair of analyses gave

Palladium, %	23.45	23.42
Carbon, %	43.79	44.33
Hydrogen, %	2.58	2.62

By comparing these results with the percentage composition of the three compounds immediately above, it is readily seen that number two, representing the formula $Pd(C_9H_6NNO_2)_2$ is identified.

The gravimetric factor for palladium in this compound is 0.2345. Instead of reducing the precipitate in a stream of hydrogen, it may be more conveniently washed free from chlorides, dried and the percentage of the metal calculated by the use of this factor.

Summary

A new quantitative method for the determination of palladium is given. The metal is removed from a chloride solution by means of a saturated solution of 6-nitroquinoline. The composition of the compound formed is $Pd(C_9H_6NNO_2)_2$, a coördinated salt in which palladium exhibits a coördination number of four. By use of the gravimetric factor, 0.2345, the percentage content of palladium may be had by direct weighing of the precipitate. The reagent does not react with the other metals of the platinum group, hence it may be used in effecting a separation of palladium from these metals.

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[9] See Clark, "A Handbook of Organic Analysis," 2d ed., Edward Arnold, London, England, pp. 191–198.