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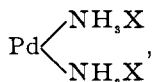
DERIVATIVES AND ATOMIC MASS OF PALLADIUM.

BY WILLETT LEPLEY HARDIN.

Received July 14, 1899.

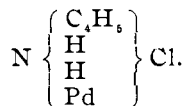
I. DERIVATIVES OF PALLADIUM.

THE ammonium derivatives of palladium have been very thoroughly investigated, and various classes of compounds have been prepared. The pallad-diammonium compounds are probably the most important of these derivatives. The constitution of this class of compounds is usually represented by the formula



where X is a univalent radical (usually chlorine, bromine, or iodine).

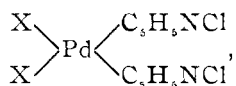
The palladium derivatives of organic bases have been investigated only to a very limited extent. In 1853 Müller¹ prepared a compound of ethylamine and palladous chloride, and suggested the formula



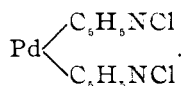
¹ *Ann. Chem.* (Liebig), 86, 366 (1853).

He also prepared the aniline derivative of palladous chloride, and described it as a yellow crystalline compound. No analyses were made of these compounds, but Müller considered them as analogous to the pallad-diammonium derivatives.

Quite recently Rosenheim and Maass,¹ have prepared a number of derivatives of pyridine with quadrivalent palladium. These compounds are represented by the formula



where X represents chlorine, bromine, or iodine. These experimenters also prepared and analyzed the compound

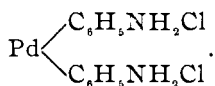


This appears to be the only derivative of bivalent palladium with an organic base, which has been analyzed. The compound was prepared by treating palladous chloride, dissolved in aqueous hydrochloric acid, with pyridine. It consists of a bright yellow crystalline powder.

In the present investigation several derivatives of bivalent palladium with organic bases have been prepared and analyzed. The compounds correspond to the pallad-diammonium salts, and are named as derivatives of these compounds.

Diphenyl-pallad-diammonium Chloride.

When a slight excess of aniline is added to a hydrochloric acid solution of palladous chloride, a voluminous yellow precipitate is formed. The compound is insoluble in hydrochloric acid, but soluble in ammonium hydroxide. When heated in a platinum spoon the substance takes fire and burns with a smoky flame. The compound is similar in appearance to the pallad-diammonium derivative, and its analysis gave results corresponding to this class of compounds. The constitution therefore may be represented by the formula



The results of the analysis are as follows :

¹ *Ztschr. anorg. Chem.*, 18, 331 (1898).

	Calculated.	Found.
Palladium.....	29.39	29.5
Chlorine	19.47	19.32

It may be mentioned also that aniline precipitates palladium quantitatively.

Diphenyl-pallad-diammonium Bromide.

This compound was prepared in a manner similar to that of the chloride; that is, by precipitating the hydrobromic acid solution of palladous bromide with aniline. The substance is similar to the chloride in appearance. The results of the analysis, and those calculated from the formula $\text{Pd}(\text{C}_6\text{H}_5\text{NH}_2\text{Br})_2$, are as follows:

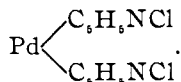
	Calculated.	Found.
Palladium.....	23.62	23.8
Bromine	35.27	35.4

Dipyridine-pallad-diammonium Chloride.

The preparation and analysis of this compound correspond exactly with the work of Rosenheim and Maass. The substance is pale yellow in color, and soluble in excess of pyridine or in ammonium hydroxide. The analysis gave:

	Per cent.
Palladium	32.0
Chlorine.....	20.8

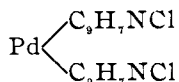
This corresponds to the formula



The theoretical values for palladium and chlorine from this formula are 32 and 21.1 per cent. respectively.

Diquinoline-pallad-diammonium Chloride.

When quinoline is added to a hydrochloric acid solution of palladous chloride a pale yellow precipitate is formed, which dissolves in excess of the quinoline to a colorless solution. On adding hydrochloric acid to the solution the substance is reprecipitated. The values obtained for the percentage of palladium and chlorine, and those calculated from the formula

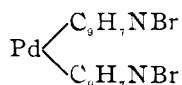


are as follows:

	Calculated.	Found.
Palladium.....	24.5	24.8
Chlorine.....	16.26	16.0

Diquinoline-pallad-diammonium Bromide.

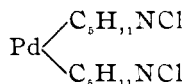
This compound was prepared from the palladous bromide and hydrobromic acid, in a manner similar to that outlined in the preparation of the chloride. Its physical properties are similar to those of the chloride. The analysis gave 20 per cent. palladium and 30.4 per cent. bromine. The theoretical values for the formula



are 20.38 and 30.05 per cent. respectively.

Dipiperidine-pallad-diammonium Chloride.

On adding piperidine to a hydrochloric acid solution of palladous chloride a pale yellow precipitate is formed, which is soluble in excess of piperidine. The substance is reprecipitated by hydrochloric acid. The palladium content was found to be 31 per cent. while that calculated from the formula

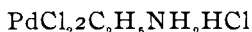


is 30.73 per cent.

The compounds which have been described are all derivatives of pallad-diammonium compounds. Hydrogen does not attack these substances at the ordinary temperature, but when brought in contact with them in a combustion tube a very small flame is sufficient to induce the reaction. The analyses were made by reducing the compounds to metal in a current of hydrogen. The volatile products were conducted into solutions of silver nitrate where the halogen content was precipitated. In order to prevent the occlusion of hydrogen the resulting metal, in every case, was allowed to cool in a current of air.

No experiments were made with the free amines of the fatty series, but one compound was prepared by a solution of palladous chloride with ethylamine hydrochloride. When the solution was partially evaporated, brownish red scales separated. These

were dissolved in water and recrystallized. The resulting crystals were analyzed and found to contain 30.3 per cent. palladium and 40.94 per cent. chlorine. The corresponding values calculated from the formula



are 31.4 and 41.58 per cent. The substance is evidently a double salt corresponding to the double chloride of ammonium and palladium.

The foregoing observations, while limited to five organic bases, indicate that bivalent palladium reacts with organic amines and other bases, in a manner similar to that with ammonia.¹ The diphenyl-pallad-diammonium chloride and the corresponding bromide can be prepared with little difficulty. Both are anhydrous and insoluble in water, and can be dried at 100° without decomposition. The compounds seem to be well adapted to atomic mass determinations.

II. THE ATOMIC MASS OF PALLADIUM.

Inasmuch as the earlier determinations of the atomic mass of palladium show considerable variation, it was thought advisable to make use of some of the compounds described in part I of this paper in a redetermination of this constant. After some preliminary observations the diphenyl-pallad-diammonium chloride and the corresponding bromide were selected as being most suitable for quantitative determinations.

Historical Statement.

In 1828 Berzelius² made the first reliable determinations of the atomic mass of palladium. The method consisted in analyzing the double chloride of palladium and potassium. The results show considerable variation. The ratio between the palladium and the potassium chloride gave 106.22 as a mean for the atomic mass of palladium.³

Sixty years later Keiser⁴ investigated the compound employed by Berzelius, and found that it contained "water of decrepita-

¹ Palladous chloride solutions were also precipitated with phenylhydrazine, but the compound was not analyzed.

² Pogg. *Ann.*, 13, 454.

³ The atomic mass of oxygen is taken as sixteen in all the calculations in this paper.

⁴ *Am. Chem. J.*, 11, 398 (1889).

tion." Keiser concluded that the potassium palladium chloride is not suitable for atomic mass determinations, and made use of pallad-diammonium chloride. The salt was carefully dried at a temperature of from 120° to 130° . The analyses were made by reducing known quantities of the substance in a current of hydrogen, and weighing the resulting metal. The mean of two series of observations gave 106.54 for the atomic mass of palladium.¹

In 1892 Keller and Smith,² investigated the various methods of purifying palladium, and concluded that the method employed by Keiser does not give a product which is free from foreign metals, especially copper. These experimenters made use of an entirely different method of purification, and probably obtained purer material than any that had been employed in the earlier determinations. After obtaining the pure metal it was converted into pallad-diammonium chloride. The material was carefully dried, and the palladium content determined by the electrolysis of the ammoniacal solution in a silver-coated platinum dish. The mean of nine determinations gave 107.18 for the atomic mass of palladium. Two experiments were made by converting pallad-diammonium chloride into palladium sulphide, by means of hydrogen sulphide. The results were about two-tenths of a unit higher than those obtained by electrolysis. The weighings were not reduced to a vacuum standard.

During this same year Bailey and Lamb³ made two series of observations on the atomic mass of palladium. They experimented with pallad-diammonium chloride, and determined both the chlorine and palladium. The chlorine determinations gave 106.65, while the palladium determinations gave only 105.75 for the atomic mass of palladium. The weighings were reduced to a vacuum standard.

In 1893, Joly and Leidie⁴ repeated the earlier determinations on the double chloride of potassium and palladium. The perfectly dry salt was dissolved in water acidulated with hydrochloric acid, and the solution electrolyzed. From the weight of

¹ This value is based upon Clarke's reductions to a vacuum standard.

² *Am. Chem. J.*, 14, 423 (1892).

³ *J. Chem. Soc.*, 61, 745 (1892).

⁴ *Compt. rend.*, 116, 147 (1893).

the metal obtained the authors gave 106.28 for the atomic mass of palladium.

During the next year Keiser and Breed¹ repeated the earlier work on the reduction of pallad-diammonium chloride. The material was carefully purified by two different methods. The mean of two series of experiments is almost identical with the value obtained by Keiser in his earlier experiments.

A glance at the foregoing results will show considerable variation. The values usually accepted for the atomic mass of palladium are as follows :

Clarke.....	106.36
Richards	106.5
German committee	106.0

No satisfactory explanation has yet been offered to account for these variations. Keller and Smith suggested that there may be a slight loss of material in the reduction of pallad-diammonium chloride. Keiser, however, in his second series of determinations, failed to detect any indications of such a loss. It has also been suggested that the high value obtained by Keller and Smith may have been due to the occlusion of hydrogen by the metallic palladium. Careful precautions, however, were taken to prevent any error from this source, and the authors were unable to detect the presence of hydrogen in the metallic deposit. The reliable determinations of the atomic mass of palladium are based almost entirely upon analyses of pallad-diammonium chloride. The variations then must be due either to the method of analysis or to the method of purifying the material. In the present investigation the metal was purified by the method of Keller and Smith, and the analyses were made in a manner similar to those of Keiser. The value obtained is higher than that usually accepted for the atomic mass of palladium. This would indicate that the results are influenced by the method of purifying the material.

Purification of Metallic Palladium.

As already mentioned the material used in these experiments was purified by the method outlined by Keller and Smith. The commercial metal, about twenty-five grams, was dissolved in

¹ *Am. Chem. J.*, 16, 20 (1894).

aqua regia, and the solution evaporated to dryness on a water-bath. The residue, after evaporating several times with hydrochloric acid, was dissolved in water containing a little hydrochloric acid. The solution was diluted with water, and treated with an excess of ammonium hydroxide. Heat was applied until the palladium salt was completely dissolved. A small quantity of reddish brown material remained insoluble. This was filtered out and the filtrate treated with an excess of hydrochloric acid, when the yellow pallad-diammonium chloride was precipitated. After standing for forty-eight hours the compound was filtered out and thoroughly washed. It was then dissolved in cold, dilute ammonia water, the solution filtered, and the palladium reprecipitated as pallad-diammonium chloride.

This salt was dried and carefully ignited in the air, after which the bluish green residue was reduced in a current of hydrogen. The resulting metal was dissolved in aqua regia and the solution evaporated to dryness on a water-bath. The residue was digested with hydrochloric acid and evaporated to dryness several times. The remaining chloride was then dissolved in water containing a little hydrochloric acid, and the solution carefully neutralized with sodium carbonate. The calculated amount of mercuric cyanide was then added, and the palladium was precipitated as palladous cyanide. After standing for several days the precipitate was repeatedly washed by decantation and finally on a filter. The palladous cyanide was dried and strongly ignited for several hours in a muffle-furnace.

The metal which resulted from the ignition of the palladous cyanide was extracted with hydrochloric acid, to remove any copper oxide that might have been present, and then dissolved in aqua regia. After repeated evaporations with hydrochloric acid, a dilute solution of the palladous chloride was saturated with sulphur dioxide. The solution became yellow in color and a slight precipitate was formed on standing. Potassium thiocyanate produced a slight turbidity when added to the yellow solution. No attempt was made to determine the composition of these precipitates.¹ Upon warming, the solution lost its color.

When the sulphur dioxide had been completely removed by

¹ In the experiments of Keller and Smith these precipitates were examined and found to contain both gold and copper.

boiling, the solution was filtered, and the palladium precipitated from the neutralized filtrate by means of potassium formate. The metal came down in black flakes. The palladium thus obtained was thoroughly washed, dried, and strongly ignited for several hours in a closed porcelain crucible in a muffle-furnace. The resulting metal after treating with hydrochloric acid was heated in a current of hydrogen, when it became almost silver-white in color.

Preparation of Diphenyl-pallad-diammonium Chloride.

Pure metallic palladium, obtained in the manner just outlined, was dissolved in hydrochloric acid containing a small quantity of nitric acid. These acids had been previously purified. The resulting solution was evaporated to dryness on a water-bath. The residue was digested with hydrochloric acid and again evaporated to dryness. This was repeated until the nitric acid was completely expelled. The resulting palladous chloride was dissolved in water acidulated with hydrochloric acid. The solution after filtering was treated with a slight excess of aniline which had been purified by several redistillations.

The resulting diphenyl-pallad-diammonium chloride was allowed to stand for twelve hours in a covered beaker. It was then washed several times by decantation, and afterward washed upon a filter. The final washings were made with alcohol. The resulting material was dried for several days at the ordinary temperature, and finally dried for forty-eight hours in an air-bath at a temperature of 90°.

Method of Analysis.

The analyses were made by reducing known quantities of the substance in a current of hydrogen, and weighing the resulting metal. The material was placed in a porcelain boat which, in turn, was placed in a hard glass combustion tube. A current of pure, dry hydrogen gas was then conducted through the tube. There was no action at the ordinary temperature, but a very small flame under the tube was sufficient to induce the reaction. The temperature was gradually increased. After the reduction appeared to be complete the temperature was kept at a bright red heat for one hour. The flames were then removed, and

when the temperature had fallen below a red heat the current of hydrogen was replaced by a current of dry air. The metal was then heated to a bright red heat for a period of two hours. This precaution was taken in order to remove any carbon which might have resulted from the decomposition. It might be remarked, however, that there were no indications of free carbon in the boat. After heating in the air the metal was again heated in a current of hydrogen, and finally cooled in a current of air to prevent any occlusion of hydrogen. The resulting metal was almost silver-white in color.

In the first experiments an attempt was made to determine the quantity of chlorine by conducting the volatile products into solutions of silver nitrate. The results, however, were not accurate enough for atomic mass determinations. The values which follow are all based upon determinations of metallic palladium. The weighings were made on a short-armed Troemner balance with a set of calibrated weights. The balance is sensitive to the fortieth of a milligram. All weighings have been reduced to a vacuum standard. In order to make these reductions the density of diphenyl-pallad-diammonium chloride was determined and found to be 1.66.

First Series.

The atomic masses used in the calculation of results are those given in Clarke's report for 1898.¹ The results from seven analyses of diphenyl-pallad-diammonium chloride are as follows :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.98480	0.28953	107.06
2	1.10000	0.32310	106.92
3	1.02820	0.30210	106.96
4	1.19230	0.35040	107.00
5	1.40550	0.41300	106.98
6	1.26000	0.37040	107.04
7	2.25510	0.66310	107.08
Mean		107.006	
Maximum			107.08
Minimum			106.92
Difference			0.16

¹ This Journal, 21, 200.

Preparation of Diphenyl-pallad-diammonium Bromide.

This compound was prepared in a manner analogous to that of the chloride. The hydrobromic acid was prepared by the action of pure bromine on anthracene. The acid fumes were conducted through tubes of anthracene to remove the free bromine. It is necessary in these experiments to use hydrobromic acid which is absolutely free from bromine, for, according to Rosenheim and Maass, these compounds take up free bromine to form addition products. This precaution was carefully observed.¹ The washing and drying of the material were carried out just as in the case of the chloride. The specific gravity of the compound was found to be 1.75.

Second Series.

Five analyses of diphenyl-pallad-diammonium bromide gave the following values for the atonic mass of palladium :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.88567	0.20917	107.01
2	1.31280	0.31000	106.99
3	1.50465	0.35540	107.03
4	2.01635	0.47635	107.05
5	2.92300	0.69080	107.10
Mean		107.036	
Maximum			107.10
Minimum			106.99
Difference			0.11

Ammonium Palladium Bromide.

This salt was prepared in a pure condition by Smith and Wallace¹ as follows: Pure metallic palladium was dissolved in nitro-hydrobromic acid. The resulting solution was evaporated, and the residue repeatedly moistened with hydrobromic acid and evaporated to dryness on a water-bath. The resulting palladium bromide was dissolved in water containing a little hydrobromic acid, and to the solution was added an equivalent quantity of ammonium bromide. On evaporating the solution large olive-

¹ Before the publication of Rosenheim and Maass had been noticed, a series of experiments were made with hydrobromic acid which contained a small quantity of free bromine. The results obtained for the atomic mass of palladium were somewhat variable, and about one unit lower than those obtained from the chloride.

² This Journal, 16, 463 (1894).

brown crystals of ammonium palladium bromide separated. The salt was dissolved in water and recrystallized. The resulting material was carefully dried, and found to be anhydrous and stable in the air. The specific gravity of the salt is 3.40.

Third Series.

This series was made with the above salt two years ago. The results of four experiments reduced to a vacuum standard are as follows :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.77886	0.18006	107.03
2	1.53109	0.35381	106.96
3	2.75168	0.63614	107.03
4	1.88136	0.43478	106.98
Mean			107.00
Maximum.....			107.03
Minimum			106.96
Difference.....			0.07

SUMMARY.

By combining the three series we obtain, as a mean of all the results, the following value :

First series.....	107.006
Second "	107.036
Third "	107.000
Mean.....	107.014

This value is higher than that usually accepted for the atomic mass of palladium. The earlier determinations are based almost entirely upon analyses of pallad-diammonium chloride, while in the present investigation new factors have been introduced. Both carbon and bromine are important elements of comparison in these determinations. Further investigation will probably be necessary to fully explain the variation in the results of the different experimenters. The fact, however, that the three series of results in the present work agree very closely with each other, and approximately with the value obtained by Keller and Smith, and the fact that there is no apparent source of error in the method employed, furnish a strong argument in favor of the

value 107 for the atomic mass of palladium. This value does not influence the position of palladium in the periodic system.

In conclusion I desire to express my obligations to Professor Edgar F. Smith for suggesting this line of work, and for many valuable suggestions during its prosecution.

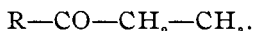
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM METHYLATE UPON DIBROMIDES OF PROPENYL-COMPOUNDS AND OF UNSATURATED KETONES.

BY F. J. POND, O. P. MAXWELL, AND G. M. NORMAN.

Received July 28, 1899.

IT was stated in a previous paper¹ that certain phenol ethers, which contain a C_3H_5 group having the propenyl structure, give bromine addition products which, on treatment with sodium alcoholate, yield ketones of the general formula,



Thus, the dibromides of anethol,² methyl-,³ ethyl-,² and benzyl-¹ isoeugenol and isosafrol³ form ketones when they are treated with sodium alcoholate. As the bromine derivatives of the corresponding isomeric compounds containing the allyl group are not converted into ketones by a similar treatment, this reaction is characteristic for those compounds containing the propenyl group. Therefore, the structure of the unsaturated group, C_3H_5 , in these two classes of compounds may be readily determined by means of this reaction.

The study of this reaction is here extended to isopiol and propyl isoeugenol, both of which contain the propenyl group, $R-CH=CH-CH_3$, and form dibromides which are readily converted into ketones; the corresponding bromine derivatives of apiol and propyl eugenol do not yield ketones when subjected to an analogous treatment.

It is also shown that the dibromides of certain unsaturated ketones represented by the formula, $R-CH=CH-CO-C_6H_5$, may be readily changed into 1,3-diketones, $R-CO-CH_2-CO-C_6H_5$. The reaction by which these diketones are formed

¹ Pond and Beers: *This Journal*, 19, 825.

² Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2714.

³ Hell and Portmann: *Ibid.*, 28, 2088; Hell and Hollenberg: *Ibid.*, 29, 682.