O. V. Shaffer

The Interaction of Platinum, Hydrochloric Acid and Hydrogen Peroxide. The reduction of Chloroplatinic Acid by Glycerol

THE INTERACTION OF PLATINUM, HYDROCHLORIC ACID AND HYDROGEN PEROXIDE. THE REDUCTION OF CHLOROPLATINIC ACID BY GLYCEROL.

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Owen Vernon Shaffer

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INTRODUCTION.

The standard method for the preparation of chloroplatinic acid, for use as a reagent in the quantitative determination of sodium, potassium and other metals, is to dissolve ignited platinum black in nitro-hydrochloric acid (Aqua-regia) (1).

$$4HNO_3 - 8HCl - Pt \text{ ——— } H_2PtCl_6 - 4H_2O - 2NO_2 - 2NOCl$$

Writers and text books have always emphasized the complete removal of the nitric acid, and the complete oxidation of the platinum to chloroplatinic acid. H_2PtCl_6 This is especially important if the chloroplatinic acid is to be used for extremely accurate quantitative work, such as the determination of the atomic weight of platinum, chlorine, or hydrogen. If the nitric acid is not completely removed by repeated evaporations with hydrochloric acid, nitro-chloroplatinic acid $H_2PtCl_4(NO_2)_2$ $H_2PtCl_5NO_2$ is formed which contaminates the product. The repeated evaporation of the chloroplatinic acid causes a slight reduction to chloroplatinous acid H_2PtCl_4, or it may also form the hydroxy-chloroplatinic acid $H_2PtCl_4(OH)_2$ H_2PtCl_5OH. In either case the product is not acid that could be used for exact analysis, thus the resulting acid is made up to volume, and saturated with chlorine gas for several hours, this causes a complete oxidation to H_2PtCl_6 and destroys any hydroxy chloroplatinic acid that has formed. The excess chlorine gas is finally removed by heating (2).

HISTORICAL.

W. A. Noyes and H. P. Weber (3) in preparing chloroplatinic acid for the determination of the atomic weight of chlorine describes an electroytic method in which the platinum black was made the anode of an electrolytic cell containing concentrated hydrochloric acid. The chlorine was liberated as nascent chlorine (Cl) in contact with the platinum black causing solution of the platinum. The dilute chloroplatinic acid thus formed was periodically drawn off and concentrated. Acid prepared in this way was free from nitric acid; but the concentrating caused a slight reduction to chloroplatinous acid, so it was necessary to oxidize the product by chlorination as described above. They were able to prepare in this way the purest chloroplatinic acid that had ever been prepared up to that time.

W. Dittman and J. McArthur (4) made chloroplatinic acid for the determination of the atomic weight of platinum by passing chlorine gas through concentrated hydrochloric acid in contact with platinum black. They report this a very tedious method.

Eurique V. Zappi (5) has prepared chloroplatinic acid free from nitro-chloroplatinic acid and completely oxidized, by dissolving sponge platinum or thin sheet platinum with hydrochloric acid and chloric acid, the chloric acid replacing the nitric acid in the nitro hydrochloric acid. (Aqua-regia). He states that the sponge platinum is as readily oxidized by hydrochloric acid , chloric acid mixture as by aqua-regia. Gold and palladium were also converted into the chlorides by the same method.

Fairly and Gmelen Kraut (6) briefly reported that hydrogen peroxide and hyrochloric acid would attack platinum without mentioning what form of platinum was used or what the resulting

products were.

C. Marie (7) reported that hydrogen peroxide appeared to be without action on platinum in either acid or alkaline solution. The reason for this was no doubt due to the physical state of the platinum used or the kind of acid used. Hydrogen peroxide will not react with platinum in acid solution unless it is acid with hydrochloric acid and most reagents will not readily oxidize platinum unless it is in the form of platinum black.

The use of hydrogen peroxide in the form of thirty percent solution (Perhydrol) for the preparation of chloroplatinic acid was suggested by P. Rudnick some years ago. In 1917 he published an article in the Journal of the American Chemical Society (8) which states specifically that hydrogen peroxide had been successfully employed as a reagent for the preparation of chloroplatinic acid. He also states that this acid gave quantitative results for the determination of sodium and poatassium.

PURPOSE OF INVESTIGATION.

This investigation was undertaken in order to determine whether chloroplatinic acid prepared by the oxidation of platinum in the presence of hydrochloric acid and hydrogen peroxide would be of sufficient purity to be used as a reagent for very accurate quantitative work. Acid prepared in this way should give potassium determinations comparable to those obtained using acid made by the standard method.

The methods suggested above seem to obviate the difficulties incurred by the presence of nitric acid when the standard method is used; however these are slow, tedious and as yet not well enough established.

The article published by Rudnick (8) on the "Preparation of Chloroplatinic Acid by means of Hydrogen Peroxide" seemed to suggest a method that had advantages over other methods, thus it seemed advisable to check the work done by Rudnick and further investigate the quality of acid produced.

THEORETICAL.

The preparation of chloroplatinic acid by the proposed method is not different in theory from the usual method, hydrogen peroxide being substituted for nitric acid as the oxidizing reagent for hydrocloric acid. Apparently any oxidizing reagent strong enough to liberate nascent chlorine (Cl) from warm hydrochloric acid may be used to prepare chloroplatinic acid.

The reaction between platinum, hydrochloric acid and hydrogen peroxide seems to be a combination of three distinct chemical reactions, first the catalytic effect of platinum black on the de-

composition of hydrogen peroxide, second the oxidation of hydrochloric acid, and third the solution of platinum black. With the oxidizing power of the hydrogen peroxide thus enhanced by the presence of the platinum black the nascent chlorine liberated readily oxidizes the platinum black. The platinum functions doubly in this reaction catalyzing a reaction in which it is being dissolved. The following equations illustrate the chemical reactions that take place.

$$H_2O_2 + Pt \rightarrow H_2O + (O)$$

$$(O) + 2HCl \rightarrow H_2O + 2(Cl)$$

$$4(Cl) + Pt \rightarrow PtCl_4$$

$$PtCl_4 + 2HCl \rightarrow H_2PtCl_6$$

$$2H_2O_2 + 6HCl + Pt \rightarrow H_2PtCl_6 + H_2O$$

At the time this work was started it was thought that perhaps the nascent chlorine liberated would not completely oxidize the platinum to chloroplatinic acid. It also seemed reasonable to expect the formation of hydroxy-chloroplatinic acids $H_2PtCl_4(OH)_2$ H_2PtCl_5OH in a solution of concentrated hydrogen peroxide. (H_2O_2 H - O ⋮ O - H) If hydrogen peroxide should have the structural formula sometimes asigned to it, it might be expected to break down to a limited extent to give two hydroxyl radicals.

MATERIAL AND METHOD OF EXPERIMENT.

It is extremely important to have platinum in the proper physical state in order to effect complete and ready solution. For this reason platinum was prepared in the following ways each product being tested with the hydrochloric acid hydrogen peroxide mixture for solubility.

Zinc-Platinum Alloy (25% Pt).(9).

Platinum was fused with zinc under a layer of suitable flux in a graphite crucible, the alloy thus obtained was treated with hydrochloric acid in which case the zinc dissolved leaving the platinum as a black powder. The platinum was washed free from zinc chloride after which it was ready for use. Platinum prepared in this way was more active in the presence of hydrochloric acid and hydrogen peroxide than ignited platinum black or sheet platinum, however it was relatively inactive and could not be used effectively in the preparation of chloroplatinic acid, besides platinum prepared in this way could not be used unless it had previously been separated from iridium and rhodium. The zinc would also require very careful purification.

Ignited Platinum Black.

Precipitated platinum black was ignited in a quartz crucible and treated with hydrogen peroxide and hydrochloric acid; but this grade of platinum was practically inert.

Platinum Black (Iridium free).

Clean sheet platinum (10) was dissolved in aqua-regia and reduced with alkaline sodium formate. The precipitated platinum black was filtered, washed and ignited. The ignited platinum was redissolved in aqua-regia in order to separate the platinum from the iridium. (Ignited iridium black is practically insoluble in aqua-regia. Iridium must be removed in this way in order to prevent contamination with chloroiridic acid H_2IrCl_6) The chloroplatinic acid was reduced a second time with alkaline sodium formate.

The precipitated platinum black thus obtained (Iridium free) was used for the preparation of all chloroplatinic acid used.

Potassium Chloride.

The best grade of commercial potassium chloride was recrystallized three times from hot water, centrifuged, heated in an oven at 150 degrees centigrade and finally fused in a platinum crucible. The fused chloride was cooled in a desiccator over lime after which a standard solution was prepared. This standard solution was checked by a silver nitrate solution previously standardized by fused sodium chloride. (Moore's Method).

Perhydrol (Hydrogen peroxide 30%).

Commercial hydrogen peroxide (3%) may be used for the oxidation of hydrochloric acid however a reagent of this strength is much less active than a more concentrated one; and besides a very large volume of reagent must be used if a large quantity of nascent chlorine (Cl) is desired. The large volume of reagent thus added would yeild a very dilute solution of chloroplatinic acid and would make necessary considerable evaporation which has a tendency to reduce the chloroplatinic acid to chloroplatinous acid. For this reason it is always advisable to concentrate the commercial hydrogen peroxide before using since it is never more than 3% and often it is even less.

All of the commercial hydrogen peroxide used as a reagent to prepare chloroplatinic acid was first concentrated in the following way.

Commercial hydrogen peroxide was distilled at 3 to 5 m.m. pressure, at a temperature of 35 to 45 degrees centigrade. The water having a higher vapor pressure at this low pressure distills off first leaving the concentrated hydrogen peroxide as a residue. On account of the instability of the hydrogen peroxide some is always decomposed, however under these conditions it is not difficult to prepare 25 to 30 % hydrogen peroxide. Peroxide of this concentration is known as perhydrol.

Four samples of perhydrol were prepared by the above method each being used to prepare chloroplatinic acid.

1st.

Commercial hydrogen peroxide (3%) was concentrated to 20 to 25%.

2nd.

Commercial hydrogen peroxide,acetanilid free,was concentrated by distilling from a quartz flask.

3rd.

Commercial hydrogen peroxide acetanilid free was concentrated by distilling from a quartz flask, the perhydrol being stored for use in paraffined reagent bottles.

4th.

Commercial hydrogen peroxide was concentrated to 25 to 30% in a pyrex distilling flask. This concentrate was removed to a quartz distilling flask and redistilled into a quartz flask. The distillate was not removed from the flask until it was to be used. The reaction between the perhydrol , hydrochloric acid and platinum black was carried out in a quartz evaporating dish.

After the hydrogen peroxide has been sufficiently consentrated and the greater part of the water driven off, the hydrogen peroxide will distill over without decomposition. At 2 to 3 m. m. pressure hydrogen peroxide is stable and will distill readily.

Apparatus.

No special apparatus was used. The distillation was carried out in the usual way, a Nelson oil pump being used to produce the vacuum.

At first pyres glass apparatus was used throughout but finally the entire apparatus was made of quartz.

Method of Experimentation.

Potassium Chloride Samples.

Ten and 20 c c portions of the standard potassium chloride solution were measured from a standardized pipette.

Determination of potassium.

The potassium chloride samples were converted into the insoluble potassium chloroplatinate by adding an excess of chloroplatinic acid reagent. The solution was then evaporated on a slow water bath (11) (the bottom of evaporating dish being portected from the direct contact of the steam by means of a piece of filter paper) until the odor of hydrochloric acid was no longer perceptible. Redistilled methyl alcohol was then added to the cooled residue and the percipitate throughly broken up with a glass stirring rod, after allowing the residue to settle, the alcoholic solution of dissolved chloroplatinic acid was decanted through a filter previously moistened with methyl alcohol.

To obviate the possible error incurred by the tendency of the alcoholic solution to "creep" up the side and over the edge of the evaporating dish,especially designed apparatus was used (12)

The washing with methyl alcohol was continued until the potassium chloroplatinate was washed free from chloroplatinic acid and sodium chloroplatinate. Three washings were sufficient in most cases to give a colorless alcoholic filtrate. The filter was allowed to stand until the methyl alcohol had completely evaporated (to save time it was often dried in an oven at 90°. If the methyl alcohol is not completely removed it will cause a slight reduction of the chloroplatinic acid to free platinum during the final evaporation) after which the decanted potassium chloroplatinate was washed through the filter into the respective evaporating dishes by means of hot water.

The potassium chloroplatinate solution was then evaporated to dryness on a slow steam bath, heated in an oven for 30-40 minutes at 130-140° centigrade, cooled in a desiccator over calcium chloride and weighed.

Theoretically (13) $\frac{2KCl}{K_2PtCl_6}$ is equal to the factor .3068 that is the weight of potassium chloroplatinate multiplied by the factor .3068 should give the weight of potassium chloride. The coefficient .3056 is used instead of the true factor .3068 because the potassium chloroplatinate precipitate does not exactly correspond to the formula K_2PtCl_6 We assume that the chloroplatinic acid is decomposed slightly during the final evaporation according to the following equation.

$$H_2PtCl_6 + HOH \rightarrow HCl + H_2PtCl_5OH$$

Thus by hydrolysis a small amount of a mixed potassium salt is obtained ($K\ H\ Pt\ Cl_5OH$) or the hydroxy salt (K_2PtCl_5OH).

Innumberable determinations have shown .3056 to be the factor to be used in calculating potassium chloride from potassium chloroplatinate.

EXPERIMENTAL DATA.

Table 1 gives results obtained using the standard potassium chloride solution and chloroplatinic acid prepared by L. S. Wells (14). This acid was prepared by the usual method i.e.dissolving ignited platinum black in aqua-regia.

While the factor obtained was not the one given by Treadwell Hall (.3056) it checked closely enough to show that the chloroplatinic acid was of high degree of purity.

This series of determinations was run preliminary to the determinations that follow, principally to check the method as outlined and also to check the technique of the writer. It also gave the writer a factor more reliable for his own work than the one given in Treadwell Hall.

TABLE I.

Wt. KCl	Wt. K_2PtCl_6	$\frac{\text{Wt. KCl}}{\text{Wt. } K_2PtCl_6}$
.2394	.7875	.3040
.2394	.7837	.3056
.2394	.7894	.3030
.2394	.7866	.3056
.2394	.7872	.3042
.2394	.7864	.3043
.2394	.7882	.3037
.2394	.7880	.3036
.2394	.7870	.3042
Average		.3049
Standard H_2PtCl_6		.3056

The above table shows very close agreement between the chemical factor actually obtained and the chemical factor given in Treadwell Hall. The factor .3049 also checks the one obtained by L. S. Wells (14) who prepared and used the same sample of acid, his factor being .3050. The value for this chemical factor had always been determined somewhat lower than the value given in Treadwell Hall; giving values between .3040 and .3050.

The following table gives results obtained using chloroplatinic acid prepared by the interaction of platinum black, hydrochloric acid and hydrogen peroxide (perhydrol). The perhydrol being made by concentrating commercial hydrogen peroxide as described.

TABLE II.

	Wt. KCl	Wt. K_2PtCl_6	$\frac{\text{Wt. KCl}}{\text{Wt. } K_2PtCl_6}$
1	.1194	.4228	.2890
2	.1194	.4264	.2865
3	.1194	.4264	.2865
4	.1194	.4270	.2796
5	.1194	.4223	.2827
6	.1194	.4038	.2957
7	.1194	.4076	.2930
8	.1194	.4056	.2944
9	.1194	.3908	.3055
10	.1194	.3975	.3004
11	.1194	.4078	.2928
	Average ----------		.2915

The chloroplatinic acid obtained had an excellent color and from all outward appearances seemed to be acid of as good quality as that used in preparing table I.

While this sample of chloroplatinic acid did not look to be different from other samples previously used there was one place in the procedure where it gave unusual results. When standard chloroplatinic acid is used the precipitated potassium chloroplatinate always completely dissolved in the hot water leaving no residue on the filter. Contrary to this, in every instance when the freshly prepared chloroplatinic acid was used the potassium chloroplatinate precipitate seemed to be homogeneous and uncontaminated until the excess chloroplatinic acid was extracted with alcohol. At this point

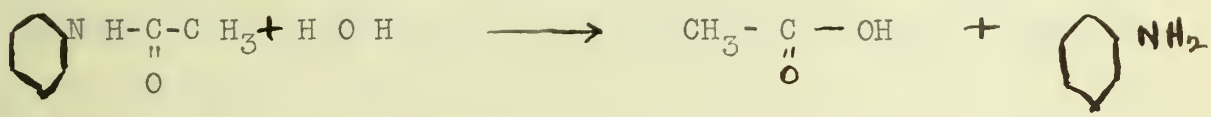
a very dark brown, finely divided precipitate came to the top and for the most part seemed to be decanted off with the wash alcohol. This dark brown insoluble residue was always very evident on the filter paper with the small amount of potassium chloroplatinate that was decanted. After the wash alcohol had been evaporated off and the decanted potassium chloroplatinate dissolved in hot water the dark brown residue still remained. This apparently insoluble residue was tested with a large volume of hot water for solubility, and it was found to be appriciably soluble. This residue being partially soluble in water and not being completely separated from the precipitated potassium chloroplatinate by decantation would account verywell for the chemical factor being low. The potassium chloroplatinate precipitate would contain in every case varying amounts of the insoluble residue thus the weight would be higher than the theoretical and the determinations would not check.

As suggested previously, the chloroplatinic acid used to prepare table II had the proper amber color, thus it seemed reasonable to assume complete oxidation, and the absence of nitro or hydroxy complexes; the presence of either of the latter always gives the acid a dark red almost bromine coloration. The apparent source of error left was the impurities that may be present in the commercial hydrogen peroxide used to prepare the perhydrol. Acetanilid for example is always added at the factory as a stabilizer to prevent decomposition. All commercial hydrogen peroxide contains small and perhaps varying amounts of acetanilid.

Perhydrol made as described above is the result of concentrating large volumes of 3% hydrogen peroxide, the perhydrol being the concentrate which always contains all of the impurities or-

iginally in the hydrogen peroxide. Thus while the hydrogen peroxide is being concentrated the impurities are also concentrated. For this reason perhydrol would contain considerable acetanilid.

Even in moderately weak alkaline solution acetanilid is readily hydrolyzed giving free aniline and acetic acid. Thus it is reasonable to assume that acetanilid would be very slightly hydrolyzed even in water solution giving the same products of hydrolysis. In case a water solution of acetanilid contains free aniline it would no doubt react with chloroplatinic acid to form an aniline chloroplatinate in the same way that it forms an aniline hydrochloride.



The amino group of aniline is sometimes used to purify gold and platinum salts.

A dilute solution of acetanilid was evaporated with an excess chloroplatinic acid and extracted with alcohol. This gave a dark brown residue insoluble in water and alcohol that compared favorably, in physical properties, with the residue obtained when the potassium chloroplatinate precipitate was extracted with alcohol. The result of this evaporation seemed to indicate that the presence of acetanilid in the perhydrol might have caused the potassium chloroplatinate precipitate to be heavy. For this reason hydrogen peroxide acetanilid free was purchased.

The next sample of perhydrol was prepared from acetanilid free hydrogen peroxide. The following results were obtained using chloroplatinic acid made from this perhydrol.

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TABLE III.

	Wt. KCl	Wt. K_2PtCl_6	$\frac{\text{Wt. KCl}}{\text{Wt. } K_2PtCl_6}$
1	.18365	.6157	.2982
2	.1810	.6050	.2993
3	.1803	.6267	.2875
4	.1806	.6188	.2919
5	.1860	.6107	.3046
6	.1804	.5935	.3040
7	.1837	.6182	.2972
8	.1812	.6041	.3000
9	.1818	.6037	.3012
	Average		.2982

The results tabulated above show a chemical factor that agrees more nearly with the results of table I than does table II, however there is still a source of error. The removal of the acetanilid had an appriciable effect on the results, thus it seemed advisable to use the acetanilid free peroxide.

A close examination of the distilling flask used to concentrate the hydrogen peroxide showed very clearly that it had been attacked by the perhydrol. This seemed to contradict a statement given in Mellor (16) (Perhydrol 25% will not attack glass unless the temperature is raised above 80 degrees centigrade). During the distillation of the hydrogen peroxide the temperature did not exceed 42 degrees however the distilling flask had been etched slightly. Since the glass contains both sodium and potassium, even though the solution of the glass was only slight, dissolved potassium would

be precipitated as potassium chloroplatinate and raise the weight of the precipitate. This would in turn reduce the value of the chemical factor.

About one hundred and fifty cubic centimeters of perhydrol were evaporated to dryness and a surprisingly heavy residue was obtained. This residue gave qualitative tests for sodium, potassium and barium in addition there was a heavy residue of silicon dioxide. This seemed to be sufficient evidence that the etching of the glass ware was responsible for the results giving a low factor; for this reason the next sample of perhydrol was prepared in quartz apparatus. The reaction between the platinum black, hydrochloric acid and perhydrol was also carrid out in a quartz evaporating dish, thus the perhydrol did not come in contact with glass in any way. The results obtained using the acid thus prepared are given in the following table.

TABLE IV.

	Wt. KCl	Wt. K_2PtCl_6	$\frac{\text{Wt. KCl}}{\text{Wt. } K_2PtCl_6}$
1	.1197	.4024	.2967
2	.1197	.4032	.2961
3	.1197	.4023	.2968
4	.1197	.3915	.3050
5	.1197	.4075	.2930
6	.1197	.4056	.2944
7	.1197	.4000	.2985
8	.1197	.4017	.2972
	Average		.2972

The results given above are practically identical with those given in table III. The error therefore can not be due to the solvent action of the perhydrol on the glass even though there is noticable etching. The amount of potassium dissolved is apparently too small an amount to effect the weight of the potassium chloroplatinate precipitate.

A sample of commercial hydrogen peroxide was evaporated to dryness and a white residue was obtained. The residue gave qualitative tests for sodium, barium, and potassium. The potassium test was not as pronounced as the other two, however considering the large volume of hydrogen peroxide that is concentrated to give a small volume of perhydrol the concentration of the potassium would have multiplied many times. It seemed necessary therefore to remove all soluble impurities in order to eliminate the possibility of introducing potassium.

Mellor states(17) that under reduced pressure, at a low temperature hydrogen peroxide is sufficiently stable to distill without decomposition. Thus after the water has distilled off the hydrogen peroxide should come over as the destillate.

The next sample of perhydrol was prepared from commercial hydrogen peroxide (containing acetanilid) by distilling from quartz into quartz, in this way removing all non-volitile impurities. A very heavy residue was formed. The chloroplatinic acid prepared from this sample of perhydrol gave the following results.

TABLE V.

Wt. KCl	Wt. K_2PtCl_6	$\frac{\text{Wt. KCl}}{\text{Wt. } K_2PtCl_6}$
.2394	.7874	.3040
.2394	.7856	.3047
.2394	.7867	.3043
.2394	.7830	.3058
.2394	.7880	.3038
.2394	.7842	.3053
.2394	.7868	.3043
.2394	.7860	.3046
.2394	.7871	.3041
.2394	.7832	.3057
Average ----------		.3045

Discussion.

The low values obtained in table II, III and IV were not caused by the partial oxidation of the platinum or by the formation of the complex molecules; but rather the soluble impurities known to be present in commercial hydrogen peroxide. In a solution nitric acid free there is no possibility of the nitro-chloroplatinic acid being formed, the solution is not evaporated to a low volume, as in other methods, so there is no chance for the formation of hydroxy chloroplatinic acid.

The data tabulated shows clearly that the removal of the acetanilid does not entirely remove the cause of the error, however when all non-volitile impurities are removed from the hydrogen peroxide potassium determinations were obtained comparable

to those obtained using a standard chloroplatinic acid.

The data herein tabulated will justify the following conclusion however the writer is aware of the fact that the commercial hydrogen peroxide used in this experimental work may or may not be a representative sample. Some samples of commercial peroxide may give slightly different results due to the amount of impurities present. It seems necessary however that they be removed.

Conclusions.

1 Hydrogen peroxide (perhydrol) and hydrochloric acid will completely oxidize platinum black to chloroplatinic acid.

2 Hydrogen peroxide (perhydrol H-O:O-H) will not react with platinum black in the presence of hydrochloric acid to form the hydroxy chloroplatinic acid in sufficient amount to interfere with the determination of potassium.

3 Commercial hydrogen peroxide can not be used to prepare chloroplatinic acid of sufficient purity to be used for very accurate quantitative work, unless all non-volitile impurities are completely removed.

REDUCTION OF CHLOROPLATINIC ACID BY GLYCEROL.

Introduction.

In this laboratory considerable quantity of chloroplatinic acid is used as a reagent, thus necessitating frequent reduction of the platinum residues. At present alkaline sodium formate is used however formerly an alkaline solution of Glycerol was used.

Treadwell Hall (18) recommends an alkaline glycerol solution for the reduction of platinum residues, and the following equation is given to represent the chemical reaction that takes place.

$$C_3H_5(OH)_3 + Na_2PtCl_6 + H_2O \longrightarrow CO_2 + NaCl + Na_2C_2O_4 + Pt.$$

Sodium oxalate being one of the products of decomposition.

Purpose of Investigation.

It had never seemed likely that oxalic acid could be formed as an oxidation product in this reaction, thus it seemed advisable to investigate carefully the products of this reaction.

Method of Experimentation.

A standard solution of glycerol was prepared by dissolving a known weight of glycerol in water. (one cubic centimeter being equivalent to .0392 gms of glycerol.) Ten cubic centimeter portions of the glycerol solution were mixed with ten cubic centimeter portions of a standard chloroplatinic acid, the solution,

made alkaline with sodium hydroxide (sp. gr. 1.2) and evaporated almost to dryness on the steam bath. This evaporation completely reduces the chloroplatinic acid precipitating the platinum in the form of a black powder.

This residue was taken up in sufficient water to cause complete solution, filtered, washed with water and finally with a few drops of hydrochloric acid. The products of decomposition are thus completely separated from the precipitated platinum black, and the latter is ready for reoxidation to chloroplatinic acid.

The filtrate from the above reaction was made acid with hydrochloric acid, to destroy the strong alkali, and warmed on the steam bath, with stirring until all of the carbon dioxide is liberated. The carbon dioxide must be completely removed in order to prevent the precipitation of calcium carbonate with the calcium sulphate solution, which is added to precipitate the oxalic acid. The carbon dioxide being removed the solution was made alkaline with ammonia hydroxide and heated to eighty degrees after which eight to ten cubic centimeters of hot calcium sulphate solution was added. In case oxalic acid is present under the above conditions it would be precipitated as calcium oxalate .

$$Ca\ SO_4 + (NH_4)_2C_2O_4 \longrightarrow Ca\ C_2O_4 + (NH_4)_2SO_4$$

The solutions remained unchanged in nearly every case however a slight precipitate appeared in several flasks. The precipitate instead of being finely divided and crystalline was heavy and flocculent. This seemed to indicate calcium carbonate instead of calcium oxalate.

The solutions were filtered through hard filters, and washed with water. The filter papers were then washed with ten to

fifteen cubic centimeters of dilute sulphuric acid and the filtrate made up to 150 c.c. volume. Five cubic centimeters of manganous sulphate solution was added, heated to boiling and titrated with standard potassium permanganate solution. Under these conditions oxalic acid, if present, would be oxidized by the potassium permanganate to Carbon dioxide, and water.

$$H_2C_2O_4 + KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$$

The following table gives the results obtained using six samples of chloroplatinic acid and glycerol.

TABLE.

Glycerol solution 1 c.c. = .0392 gms.glycerol

10 c.c. H_2PtCl_6 = 2 c.c. glycerol

	H_2PtCl_6	$C_3H_5(OH)_3$	NaCH	$KMnO_4$
1	10 c.c.	10 c.c.	10 c.c.	.03 c.c.
2	10 "	10 "	10 "	.05 "
3	10 "	10 "	10 "	.06 "
4	10 "	10 "	10 "	.06 "
5	10 "	10 "	10 "	.06 "
6	10 "	10 "	10 "	.06 "

Theoretically the ten cubic centimeter portion of glycerol solution should have given sufficient oxalic acid to reduce about thirty-nine cubic centimeters of potassium permanganate solution. The volume of potassium permanganate solution actually used however was only that amount required to give an end point on a blank solution.

In each of the above determinations an excess of glycerol was used. Theoretically only 2 c. c. of the glycerol solution would

have been necessary for the reduction however 10 c. c. was added. Since there was no oxalic acid formed in the presence of an excess of glycerol it would not be formed in the presence of an excess of the oxidizing reagent (H_2PtCl_6).

Alkaline sodium oxalate was evaporated with chloroplatinic acid in the manner described for glycerol and it also reduced the chloroplatinic acid to platinum black, thus sodium oxalate could not be expected as one of the products of the glycerol oxidation.

CONCLUSION.

Sodium oxalate is not formed as a decomposition product when chloroplatinic acid is reduced by alkaline glycerol solution, unless it is formed as an intermediate product in the reaction.

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