Ketene reacts much more slowly with water than with aniline or with toluidine.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. III. PREPARATION AND PROPERTIES OF THE OXIDE OF PLATINUM OBTAINED BY THE FUSION OF CHLOROPLATINIC ACID WITH SODIUM NITRATE[1]

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In two previous papers[3] the platinum oxide obtained by the fusion of chloroplatinic acid and sodium nitrate has been shown to be an excellent catalyst in the reduction of organic compounds. This method for the preparation of an oxide of platinum is new. The chemical nature of this oxide and a quantitative study of the best conditions for its preparation have not yet been described.

This communication discusses (1) the best fusion temperature for preparing the platinum oxide of highest catalytic activity; (2) the quantitative analysis of various samples of the catalyst prepared at different temperatures; (3) the general chemical properties of the oxide; (4) a comparison of the activity as a catalyst of the oxide of platinum prepared from chloroplatinic acid by fusion with sodium nitrate and by fusion with the nitrates of other metals; (5) a comparison of the catalytic activity of the oxide made by the sodium nitrate fusion method with the oxides of platinum prepared by methods which have already been described in the literature.

The Temperature of Fusion

The best qualitative conditions for preparing the oxide of platinum have been described; a large excess of nitrate is advisable, and a rather high temperature of fusion gives a more active catalyst. During the fusion fumes of nitrogen dioxide are evolved and the oxide of platinum is precipitated. It is probable that the following reactions take place: $6NaNO_3 + H_2PtCl_6 \longrightarrow 6NaCl + Pt(NO_3)_4 + 2HNO_3$; $Pt(NO_3)_4 \longrightarrow PtO_2 + (NO_2)_4 + O_2$.

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[2] This communication is an abstract of a thesis submitted by R. L. Shriner in partial fulfilment of the requirements for the Degree of Master of Science in Chemistry at the University of Illinois.

[3] (a) Voorhees with Adams, THIS JOURNAL, **44,** 1397 (1922).
(b) Carothers with Adams, *ibid.,* **45,** 1071 (1923).

The standard procedure used to determine the temperature of fusion that gives the most active catalyst was similar to that previously used. A solution of 4.2 g. of chloroplatinic acid in 10 cc. of water was mixed with 40 g. of c. p. sodium nitrate and evaporated to dryness in a casserole or beaker. The mass was then heated with an ordinary Bunsen or Meker burner until fusion took place. The mixture and melt were stirred continuously with a thermocouple encased in a Pyrex glass tube and the temperature was read on a pyrometer. After the fusion was complete, the melt was allowed to cool and treated with water until the filtrates were free from nitrates and nitrites. The oxide was then dried in a desiccator and weighed in order to determine the yield. Portions of this dried material were weighed for the reduction experiments.

The temperatures used in the fusion for the preparation of the oxide ranged from 310°, the lowest possible temperature, to 700°, a temperature which is bright redness and cannot be reached with two Bunsen burners; it is necessary to use at least one Meker burner and one Bunsen burner.

In the first experiment the mixture was heated, during the course of 5 minutes, to 270–280° at which temperature melting began. The temperature was gradually raised, the reaction mixture reaching 300° at the end of about 8 minutes, and evolution of nitrogen dioxide commenced. The heating was continued until at the end of 10 minutes it reached 310°, then it was increased rapidly to 320° where it was held until the end of 20 minutes, after which the mixture was allowed to cool. Gas was evolved slowly from the time a temperature of 300° was reached and at the same time a brown precipitate gradually appeared. The reaction mixture was then worked up as described and the yield of 0.3 g. (1.69 g. is the theoretical amount) of platinum oxide was obtained. It is obvious that under these conditions the reaction was not nearly complete.

In the second experiment, the mixture was heated more rapidly, the fusion reaching 350–370° in 10 minutes. At this temperature a very vigorous evolution of oxides of nitrogen took place. The temperature was raised to 400° by the end of 15 minutes, by which time the evolution of gas had slackened. The temperature was then held at 400° until 20 minutes had elapsed when heating was discontinued. Evolution of gas had practically stopped at the end of this time. The precipitation of the oxide of platinum was rapid from 350° on. The yield of dry product was 1.4 g.

In the subsequent experiments sufficient heat was applied so that a temperature of 350–370° was reached in 10 minutes. The temperature was then raised and controlled over the period between 10 and 25 minutes. In each case, at the end of 15 minutes the evolution of gas had almost stopped. In Expt. 3, a temperature of 400° was reached at the end of 15 minutes and a temperature of 490–500° at the end of 20 minutes, at which point it was maintained until 25 minutes had elapsed.

In Expt. 4 the temperature was about 500° at the end of 15 minutes, 580° at the end of 20 minutes, and was maintained at 590–600° until 25 minutes had elapsed.

In Expts. 5 and 6 the conditions were similar to those in Expts. 3 and 4, except that in Expt. 5 a temperature of 650°, and in Expt. 6 a temperature of 700° was reached at the end of 20 minutes and maintained at this point until 25 minutes had elapsed. At a temperature of 650° and higher the melt boiled.

The yield of oxide in Expts. 3, 4, 5, 6 was practically quantitative. The only difference in the oxides obtained at the different temperatures was in their appearance, the color changing from light brown in Expts. 1 and 2 to a very deep brown in Expt. 6.

In order to determine the relative activity of the various samples of oxide as catalysts, standard experiments were carried out with each sample in the reduction of two different types of organic compounds, benzaldehyde in the presence of a trace of ferrous chloride, and maleic acid. The procedure was to dissolve 20 g. of benzaldehyde or 20 g. of maleic acid in 150 cc. of 95% alcohol. To the benzaldehyde solution in each case, was added 1 cc. of 0.0001 *M* ferrous chloride.[3b] The solutions were reduced with 0.25 g. of catalyst in exactly the same manner as described in a previous paper.[3b] Table I gives the time for the reduction in each case.

TABLE I

COMPARISON OF CATALYTIC ACTIVITY IN REDUCTION EXPERIMENTS OF SAMPLES OF OXIDE MADE AT DIFFERENT TEMPERATURES

Catalyst sample	Maximum temperature of fusion ° C.	Time for reduction in minutes after reduction started Benzaldehyde	Maleic acid
1	310–320	40	..
2	390–400	22	10
3	490–500	10	11
4	590–600	11	19
5	650	20	17
6	700	20	16

The lag in the conversion of the platinum oxide to platinum black differed in each sample of the catalyst. It has not been taken into account in Table I but is shown in Table II. To find the total time, therefore, which is necessary for the reduction of benzaldehyde or maleic acid from the time the platinum oxide catalyst was added, it is necessary to add to the time given in Table I the corresponding lag time given in Table II.

TABLE II

COMPARISON OF TIME OF REDUCTION TO PLATINUM BLACK OF SAMPLES OF OXIDE MADE AT DIFFERENT TEMPERATURES

Catalyst sample	Maximum temperature of fusion ° C.	Time elapsing before platinum oxide was reduced to platinum black Benzaldehyde Min.	Maleic acid Min.
1	310–320	10	..
2	390–400	5	2
3	490–500	1	1
4	590–600	2	3
5	650	7	5
6	700	11	17

These experiments show that a temperature of about 500° is most satisfactory for the fusion in order to obtain a catalyst of maximum activity and minimum lag. For this temperature one Bunsen burner turned on as high as possible was necessary. They also show that any sample of catalyst may have a slightly variable lag depending upon the compound to be reduced; it may be possible, however, that this is due to slight changes in the conditions of the experiment. It is difficult to determine the lag accurately so that little importance can be given to slight differences in these values. In the previous papers describing the use of this catalyst, reactivation with air has been recommended in order to get the maximum speed of reduction of the organic compounds. It has been found since the publication of the first two papers that reactivation of the catalyst with oxygen instead of with air, as suggested by Willstätter[4] has a much greater effect than had been anticipated. It is advisable, therefore, whenever using this catalyst, to reactivate by the latter method just mentioned. It is conceivable that in the reduction of a few types of organic compounds this would not be possible, but in the large majority it is possible, and will greatly cut down the time of the reaction.

The results on the activity of the platinum oxide catalyst made at different temperatures differ from those described in the first paper by Voorhees and Adams. This discrepancy in regard to the proper temperatures of preparation and speed of reduction is due to the fact that the reduction of benzaldehyde was chosen as a standard for the determination of the efficiency of the catalyst. At that time the tremendous effect of small amounts of certain metallic salts upon the activity of the platinum catalyst in the reduction of aldehydes was not known and consequently care was not taken to use platinum catalyst from the same source in every experiment.

Quantitative Analysis

Qualitative tests showed that the oxide of platinum obtained in the manner described contained a certain amount of water which probably was taken up during the washing to remove the alkali salts; the oxide also contained small amounts of alkali salts which were included and could not be washed out. The quantitative analyses showed the oxide to be $PtO_2.H_2O$.

The general procedure for the quantitative analyses was to heat weighed samples (about 0.5 g.) that had been previously well dried in a vacuum desiccator, to bright redness in a porcelain boat in a glass tube heated by an electric combustion furnace. Carbon dioxide was passed through continuously during the heating and the water that was driven off was absorbed in a sulfuric acid tube. After about 1 hour at bright redness no more moisture was evolved, the bulb was removed and the weight of water determined. The carbon dioxide was now stopped and hydrogen was passed over the red-hot residue in order to reduce the oxide to metallic platinum. This procedure was continued for 1.5 hours when no more moisture was formed. The boat was then allowed to cool and was weighed.

[4] Willstätter, *Ber.*, **54**, 113 (1921).

The value thus obtained represented metallic platinum plus any alkali salts which were present. The residue was boiled with dil. sulfuric acid,[5] the platinum filtered, dried and weighed. This treatment extracted practically all of the alkali salts.

It was found also that the catalyst contained a small amount of glaze from the porcelain casserole when such a vessel was used for the fusion. This was determined by dissolving a sample of the oxide in constant boiling hydrobromic acid, filtering the solution through a Gooch crucible and weighing the insoluble residue. This glaze averaged about 0.0025 g. in each 0.5g. sample and did not vary appreciably in the various samples of oxides.

The completed results on the analysis of each of the samples of catalyst, prepared at the various temperatures, are given in Table III.

TABLE III

QUANTITATIVE ANALYSES OF SAMPLES OF OXIDE MADE AT DIFFERENT TEMPERATURES

Temperature ° C.	% Pt	% H_2O	% Alkali salts
390–400	78.90	7.13	2.22
490–500	79.80	7.37	1.72
590–600	78.00	9.16	3.56
650	79.80	8.83	3.66
700	79.40	8.06	4.80

Calc. for $PtO_2.H_2O$: Pt, 79.95; H_2O, 7.34.

It may be seen that the amount of alkali salts varied with each preparation and particularly that the amount of alkali salts increased with the higher temperatures. Moreover, it is noticeable that the moisture content was somewhat higher with the oxides made at the higher temperatures. Although the analyses vary somewhat from the calculated results, they check much more closely with the theoretical values than many of the analyses of the oxides of platinum prepared by other investigators. The analyses leave no doubt as to the constitution of the oxide.

Properties of the Oxide

The physical and chemical properties of this oxide of platinum are interesting. It has already been mentioned that the color varied with the temperature at which the fusion was made. At the lowest temperature it was a very light brown and darkened gradually until at the highest temperature it was a very deep brown. It is probable that the difference in the color is due merely to a difference in the size of particles. A microscopic examination showed that the oxide is in every case non-crystalline in character and is composed of amorphous, approximately round granules.

The oxide dissolved only slightly in hot aqua regia even after long heating. It was insoluble in boiling concd. nitric acid and only slightly, or

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[5] Wöhler and Martin, *Z. Elektrochem.*, **15**, 132 (1909).

at least only slowly, soluble in boiling concd. hydrochloric acid. On the other hand, constant boiling hydrobromic acid dissolved it completely and instantly in the cold with the evolution of bromine and the formation of bromoplatinic acid which could be readily precipitated as the red potassium salt.[6] By boiling it with 10% hydrobromic acid, solution was readily effected. It seems probable that the hydrobromic acid first reduces the dioxide to the monoxide which is dissolved with the formation of platinous bromide and then reoxidized by the bromine to the platinic bromide. Dilute or concd. hydrochloric acid had very little effect alone, but when a very small amount of sulfur dioxide was bubbled through dilute hydrochloric acid this mixture dissolved the platinum oxide rapidly and completely upon warming. In this case the reduction of the dioxide to the monoxide undoubtedly took place first before solution resulted. Other reducing agents with the dilute hydrochloric acid would undoubtedly produce the same effect.

The oxide caused the immediate decomposition of hydrogen peroxide without itself being apparently changed. When boiled with ethyl alcohol out of contact with air, the oxide was gradually reduced and acetaldehyde was formed.

Effect of the Nature of the Nitrate on the Activity of the Catalyst

All of the nitrates of the other alkali metals and of the alkaline earth metals fuse below 650°. These were, therefore, substituted for sodium nitrate in the fusion of the chloroplatinic acid. The oxides thus obtained were compared as catalysts by studying the reduction of benzaldehyde in exactly the same manner as previously described.

The procedure for these fusions was essentially the same as with sodium nitrate except that 3 g. of chloroplatinic acid and 20 g. each of the nitrates were used. The temperature was determined in a similar manner and the melt also treated similarly. The yields of product were quantitative in every case. In Table IV the results of these experiments are given.

Table IV

Comparison of the Catalytic Activity in Reduction Experiments of Samples of Oxide by the Use of Various Nitrates

Nitrate	M. p. ° C.	Time for reduction of benzaldehyde after reduction started Min.	Time for reduction of oxide to platinum black Min.	Temp. of fusion ° C.
$LiNO_3$	253	12	9	490–500
$NaNO_3$	312	10	1	490–500
KNO_3	337	25	3	490–500
$Ca(NO_3)_2$	561	80	58	500–530
$Ba(NO_3)_2$	575	135	28	600–630
$Sr(NO_3)_2$	645	No reduction	..	630–640

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[6] Billmann and Anderson, *Ber.*, **36**, 1566 (1903).

The lithium nitrate worked very satisfactorily in the fusion and yielded an active catalyst. It is noticeable, however, that the oxide produced is reduced to platinum black more slowly than that obtained by fusion with sodium nitrate.

The potassium nitrate was not so satisfactory as sodium nitrate. During the evaporation of the mixture of chloroplatinic acid and potassium nitrate to dryness, excessive foaming took place caused probably by the precipitate of potassium chloroplatinate. The oxide of platinum was produced in good yields but was not so active a catalyst as that obtained by the use of sodium nitrate.

Calcium nitrate itself decomposes just above its melting point into calcium nitrite and then into calcium oxide so that during the fusion with chloroplatinic acid the melt became very thick and viscid. The catalyst produced was very light yellow in color and did not resemble the oxide obtained by the fusion with the alkali metal nitrates. It was rather fluffy in appearance. It seems probable that this was an oxide of the formula $PtO_2.2H_2O$, since it resembled in appearance this substance as made by a method described in the literature and also in its catalytic activity in reduction experiments. The production of this substance could be explained by the primary formation of the calcium oxide which would precipitate the platinum oxide just as sodium hydroxide precipitates it from the chloroplatinic acid.

Both barium and strontium nitrates melt at so high a temperature that the platinum chloride, for the most part, is decomposed to metallic platinum before the fusion occurs, and hence the products from these fusions would not be expected to be so active as catalysts. That obtained from the barium nitrate caused the reduction of benzaldehyde only very slowly, and that from the strontium nitrate caused no reduction at all.

Comparison of this Catalyst with Platinum Oxides Made by Other Methods

A discussion[3a] has already been made of the reasons for attempting to use the oxides of platinum as catalysts in the reduction of organic compounds. None of the oxides is as conveniently prepared as the oxide prepared by the fusion of sodium nitrate and chloroplatinic acid. Wöhler and Martin[5] gave explicit directions for the preparation of a number of the oxides and these directions have been followed. These investigators, however, did not mention yields, a point of considerable importance when the oxides are to be used as catalysts. Most of the methods consisted in wet precipitation, and as slight changes in condition might make a considerable difference in the activity of the product as a catalyst, two different samples of each oxide were prepared.

In Table V a summary of the results of the use of PtO_2, $PtO_2.2H_2O$,

Pt_2O_3, Pt_3O_4 and $Pt(OH)_2$ in reduction experiments is given. Since the majority of the oxides were comparatively non-active catalysts, smaller amounts of maleic acid and benzaldehyde were reduced than when the oxide catalyst prepared by fusion was used.

Table V

Comparison of Catalytic Activity in Reduction Experiments of Fusion Oxide and Various Platinum Oxides Made in Other Ways

			Total time for reduction including reduction of oxide to platinum black			
			Maleic acid (10 g.)		Benzaldehyde (with $FeCl_2$) (9.5 g.)	
Oxide	% of oxide obtained from the chloroplatinic acid used	Amount of oxide used G.	Sample 1	Sample 2	Sample 1	Sample 2
Fusion oxide....	100	0.25	10 m.	...	7 m.	...
PtO_2...........	51	.24	4 h.	1.25 h.	50 m.	69 m.
$PtO_2.2H_2O$......	60	.30	5.66 h.	5.0 h.	40 m.	60 m.
Pt_2O_3..........	6	.23	5.5 h.	No red.	3.5 h.	4.75 h.
Pt_3O_4..........	82	.23	2.3 h.	2.6 h.	1.41 h.	1.33 h.
$Pt(OH)_2$........	14	.24	No red.	No red.	8.41 h.	32 h.

It is noticeable that the yields of these other oxides were not nearly so satisfactory as that obtained by the fusion method. The oxides, moreover, were not nearly such active catalysts and the same oxide varied in activity from sample to sample even though prepared by the same directions. One of the distinct advantages in the fusion oxide is that a catalyst of standard activity is obtained.

The oxide Pt_3O_4 was made by the fusion of chloroplatinic acid with sodium carbonate. The oxide was formed in satisfactory yields distinctly greater than those of the oxides prepared by any of the other methods except that by fusion with sodium nitrate. The activity as a catalyst, however, was not as great as with PtO_2 or $PtO_2.2H_2O$.

In Table V the times recorded include both the time of reduction of the oxide to platinum black and the time of reduction of the compound. Since the last 3 oxides in the table were black at the beginning, it was very difficult to determine the exact point at which a platinum black was formed and consequently in order to have uniform results for comparison the total time was recorded.

Summary

1. The fusion of sodium nitrate and chloroplatinic acid has been carried out at various temperatures between 310° and 700°. The various samples of oxide of platinum produced were tested as catalysts in the reduction of maleic acid and benzaldehyde. It was shown that the oxide prepared at about 500° gave the best results in the reduction experiments.

2. A quantitative analysis of the oxide has shown it to have the composition $PtO_2.H_2O$.

3. This oxide is insoluble in aqua regia, concd. nitric or concd. hydrochloric acid. It is readily soluble in hydrobromic acid or hydrochloric

acid containing reducing agents such as sulfur dioxide. It decomposes hydrogen peroxide without itself being changed. It oxidizes alcohols to the corresponding aldehydes.

4. It has been shown that the nitrates of lithium, potassium, calcium, barium and strontium are not nearly so satisfactory for the fusion with chloroplatinic acid as sodium nitrate.

5. A comparison of the catalytic activity of this oxide with the various oxides obtained by methods described in the literature has shown the former to be far superior. Moreover, it is much more readily prepared.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE[1] AND THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CONSTITUTION OF CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM. III

BY E. K. NELSON AND L. E. DAWSON

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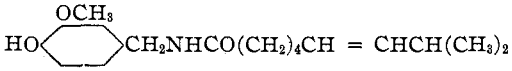
In former contributions by one of us[2] capsaicin was shown to be the vanillyl amide of a decenic (decylenic) acid. Beyond proof that this decenic acid is not a straight-chain acid, its constitution remained undetermined. The primary purpose of the present work was to determine the structure of this acid, thereby establishing the complete structure of capsaicin.

On account of the scarcity of material at the time, it was decided to attack the problem from the synthetic end, which required, of course, the synthesis of a considerable number of 10-carbon acids. In order to simplify the work, the question of the location of the double bond was deferred for the time being, and a saturated acid was sought which, when condensed with vanillyl amine, would give a product identical with that obtained on hydrogenating the side chain of capsaicin.

Such an acid was finally found in 8-methyl-nonoic acid, which has been described by Levene and Allen.[3]

The location of the double bond in the decenic acid from capsaicin was finally determined by its oxidation with a 5% solution of potassium permanganate, the products being adipic acid and *iso*butyric acid.

This shows that the double bond is located between the sixth and seventh carbon atoms, and that capsaicin is the vanillyl amide of Δ^6, 8-methyl-nonenic acid,



$$\overset{OCH_3}{HO\langle\quad\rangle}CH_2NHCO(CH_2)_4CH = CHCH(CH_3)_2$$

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[1] Released by Chemical Warfare Service.

[2] Nelson, THIS JOURNAL, **41,** 1115 (1919); **42,** 598 (1920).

[3] Levene and Allen, *J. Biol. Chem.*, **27,** 433 (1916).