



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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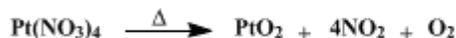
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.463 (1941); Vol. 8, p.92 (1928).

PLATINUM CATALYST FOR REDUCTIONS

[Platinic oxide]



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1. Procedure

In a porcelain casserole (a Pyrex beaker may be used) is prepared a solution of 3.5 g. (Note 1) of a commercial c.p. chloroplatinic acid (Note 2) and (Note 3) in 10 cc. of water, and to this is added 35 g. of c.p. sodium nitrate (Note 4). The mixture is evaporated to dryness by heating gently over a Bunsen flame while stirring with a glass rod. The temperature is then raised, 350–370° being reached within about ten minutes. Fusion takes place, brown oxides of nitrogen are evolved, and a precipitate of brown platinum oxide gradually separates. During this procedure foaming often occurs, in which case the mass must be more vigorously stirred and an additional flame directed at the top of the reaction mixture. If the burner under the casserole is removed when foaming starts, the top of the fused mass solidifies and foaming may become sufficient to carry material over the sides of the casserole. By the end of fifteen minutes, when the temperature has reached about 400°, the evolution of gas has greatly decreased. At the end of twenty minutes the temperature should be 500–550°. At this point the vigorous evolution of oxides of nitrogen has practically ceased, and a gentle evolution of gas takes place. The temperature is held at this point (best with the full force of the burner directly on the casserole) until about thirty minutes have elapsed, when the fusion should be complete. This temperature (500–550°) is most satisfactory for the fusion (Note 5) in order to obtain a catalyst of maximum activity and minimum lag (Note 6). The temperature indicated is generally attained by means of one ordinary Bunsen burner turned on as high as possible; where the gas pressure is lower a Meker burner may be necessary.

The mass is allowed to cool and is then treated with 50 cc. of water. The brown precipitate settles to the bottom and can be washed by decantation once or twice, then filtered (preferably through a hardened filter paper on a Gooch crucible), and washed on the filter until practically free from nitrates. If the fusion has been properly carried out no difficulty is encountered in this procedure; but if the temperature of fusion has not been high enough or has not been maintained for a sufficiently long time the precipitate tends to become colloidal on addition of water and does not filter well; moreover, under these conditions, the yield of product and its activity as a catalyst are diminished. Sometimes the precipitate becomes colloidal only when practically all the nitrates are removed; in this case it is better to stop washing as soon as the colloid starts to form, since small traces of the salt do not affect the efficiency of the catalyst. The filtrates should be tested for platinum and saved if any is present (Note 7). The oxide is either used directly, or more generally it is dried in a desiccator and portions of the dried material weighed out for reductions. The yield is 1.57–1.65 g. (95–100 per cent of the theoretical amount) (Note 5) and (Note 8). The use of platinum oxide is illustrated in the reduction of ethyl *p*-nitrobenzoate to ethyl *p*-aminobenzoate (p. 240) and of benzalacetophenone to benzylacetophenone (p. 101).

The platinum black by reduction of the oxide may sometimes be used a second, third, or even more times in the reduction of certain compounds merely by reactivating (Note 9) with air or oxygen. A spent catalyst must be reworked (Note 3) along with the platinum recovered from filtrates (Note 7), filter papers (Note 10) and the casserole (Note 11). In the use of platinum oxide-platinum black for reductions, certain types of compounds require different physical conditions from others in order to obtain the best results in each case, and factors such as the following must be taken into consideration: the temperature, the medium in which the reduction of platinum oxide to platinum black occurs (Note

12), the effect of traces of inorganic salts (Note 13), and the solvent employed (Note 14). Palladous oxide-palladium black has been used for catalytic reduction, and in some cases has proved a more efficient catalyst than the platinum oxide-platinum black, though generally this has not been found true (Note 15).

2. Notes

1. If a considerable quantity of platinum oxide is desired it is more satisfactory to prepare several runs of the size indicated than one large run, since spattering and the evolution of gases make large amounts inconvenient to handle. The activity of the catalyst appears in certain cases to decrease after standing for several weeks and therefore the oxide should preferably be prepared as required.

2. Commercial c.p. chloroplatinic acid varies somewhat in its purity. In this work that from the Mallinckrodt Chemical Works, St. Louis, was used and gave very satisfactory results. Since small amounts of impurities in the catalyst are important factors in the rate of reduction of certain types of compounds, this question of impurities in the chloroplatinic acid must be taken into account (Note 13). In a large proportion of the reductions studied, platinum oxide prepared from the chloroplatinic acid mentioned gave as good results as that from spectroscopically pure chloroplatinic acid made according to the directions of Wichers.¹

If only platinum metal is available this is dissolved in aqua regia and evaporated to dryness several times with hydrochloric acid, until free from nitrates (Note 3) and the product purified according to the method of Wichers.

3. Platinum residues may be reworked by dissolving them in aqua regia, filtering, evaporating the filtrate to dryness, taking up with a little water, and fusing with sodium nitrate. If organic matter is present in the chloroplatinic acid, as it generally is when recovered platinum is used, it will be oxidized during the fusion and, except in cases requiring a spectroscopically pure platinum, seems to have no deleterious effect. Repeated reworking does seem to cause an accumulation of poison in the catalyst, and under these conditions it should be purified as described by Wichers.¹

The following alternative procedure for the preparation of the catalyst is particularly time-saving when scrap platinum or spent catalyst is used, for after conversion to chloroplatinic acid a purification is conveniently effected by precipitating the ammonium salt, and the direct fusion of this salt with sodium nitrate eliminates the tedious process of reconversion to chloroplatinic acid. Furthermore ammonium chloroplatinate is not hygroscopic and can be weighed accurately. The amount of catalyst obtained is almost exactly half the weight of the ammonium salt employed.

A mixture of 3 g. of ammonium chloroplatinate and 30 g. of sodium nitrate in a casserole or Pyrex beaker is heated gently at first until the rapid evolution of gas slackens and then more strongly until a temperature of 500° is reached. This operation requires about fifteen minutes, and there is no spattering. The temperature is held at 500–520° for one-half hour and the mixture is then allowed to cool. The platinum oxide catalyst, collected in the usual way by extracting the soluble salts with water, weighs 1.5 g. and is comparable in appearance and in activity to the material prepared from chloroplatinic acid. [William F. Bruce, private communication, and J. Am. Chem. Soc. **58**, 687 (1936). Checked by L. F. Fieser, R. P. Jacobsen, and M. S. Newman.]

4. u.s.p. sodium nitrate could probably be used in place of the c.p. grade in most instances, but in one type of reduction at least (that of aminophenols to cyclic amino alcohols) the small amount of impurities in the u.s.p. grade affected the activity of the catalyst. It has been reported that the use of potassium nitrate instead of sodium nitrate yields a more active catalyst.²

5. The relation of temperature of fusion to the properties of the catalyst produced was determined³ by carrying out the fusion at various temperatures, which were recorded by stirring continuously with a thermocouple encased in a Pyrex glass tube, and reading the temperature on a pyrometer. The product prepared at lower temperatures is usually light brown in color and has a greater tendency to become colloidal on washing. The catalyst prepared at intermediate temperatures is brown; at 600° it is a very deep brown. The color may vary even when the catalyst is prepared under conditions which are essentially the same, but if the temperature indicated in the procedure is used the oxide will be satisfactory.

The products prepared at temperatures below 450° and above 600° have a lower activity and require a longer time for reduction to platinum black than those prepared at temperatures between 450° and 600°. If the fusion temperature is about 300°, the yield of platinum oxide is very low; at higher temperatures

the yield increases; and at temperatures of 450° and above it is practically quantitative. With a proper fusion a slightly lower yield than quantitative is generally not due to non-precipitation of the platinum but to loss by spattering and to deposition of a small amount on the casserole.

It has been suggested⁴ that the fusion be conducted in a Pyrex beaker or casserole resting in a cavity in a copper block heated with a burner and provided with a thermometer well. This permits more accurate temperature control and is claimed to furnish a catalyst of maximum and reproducible activity.

6. The brown oxide is a heavy granular powder which settles to the bottom of the solution in the bottle in which the reduction is carried out (p. 61). It must be reduced to platinum black before it becomes a catalyst for the reduction. When the hydrogen is admitted and the bottle shaken the brown oxide becomes black and whips up into a fine suspension. The time necessary for the change of the oxide to platinum black is called the lag. The lag varies usually from several seconds to two or three minutes, depending upon the conditions under which the platinum oxide is reduced to platinum black. In general the lag is short provided that the reduction of the oxide is carried out merely in the presence of solvent; if carried out in the presence of solvent and substance to be reduced, as is more common practice, the character of the substance being reduced has a considerable effect, and sometimes a lag of ten to fifteen minutes occurs. In experiments where foreign salts are added as promoters or poisons, the lag varies widely, though generally within a maximum of ten to fifteen minutes; exceptions occur, and it was found that the lag was forty to sixty minutes or more when the platinum oxide was reduced in the presence of a little sodium nitrite and an alcoholic solution of benzaldehyde. It is probable also that the temperature at which the platinum oxide is formed from the chloroplatinic acid and the solvent present have some effect on the ease with which it is reduced to platinum black.

7. It is advisable to test for platinum in all the filtrates before discarding any of them, since there is sometimes a tendency for small amounts of platinum to remain in solution. A very satisfactory and delicate test for platinum, described by Wöhler,⁵ consists in making the solution acid with hydrochloric acid and adding a few drops of stannous chloride. A yellow color develops when platinum is present and a brown color when it is in large amount. If any doubt exists as to whether or not the solution is yellow, it should be shaken with a small amount of ether; the yellow color concentrates in the ether layer, indicating the presence of platinum. From the sodium nitrate filtrates a large proportion of the platinum can be recovered by adding excess of formaldehyde and sodium hydroxide and heating. Upon standing, platinum black separates and may be filtered and worked up with other platinum black residues. The platinum which still remains in solution after this precipitation can be recovered by acidifying the solution and heating with zinc.

8. Quantitative analyses show the oxide to be $\text{PtO}_2 \cdot \text{H}_2\text{O}$.³ It usually contains a very small amount of glaze from the casserole, but this does not affect its use or activity. The oxide dissolves only slightly in hot aqua regia even after long heating; it is insoluble in boiling concentrated nitric acid, and only slightly, or at least only slowly, soluble in boiling concentrated hydrochloric acid. Constant-boiling hydrobromic acid, on the other hand, dissolves it completely in the cold with the evolution of bromine and the formation of a solution of bromoplatinic acid from which the red potassium salt can be readily precipitated or the solution may be evaporated and the residue used directly in a subsequent fusion.

9. The platinum oxide-platinum black, like any other platinum black, gradually loses its activity with use. In the reduction of certain types of compounds, notably aldehydes, the catalyst can be revived by shaking with air or oxygen for a few minutes.⁶ Frequently this must be done in order to have the reduction go to completion, and often it is desirable to do so during a reduction so as to increase the rate of reaction. In other reductions, attempted reactivation as described results in the complete inactivation and frequently the coagulation of the catalyst. In reducing certain substances, the catalyst tends to coagulate in lumps during the reduction, particularly toward the end of the reduction. In these instances reworking of catalyst is necessary (Note 3) before it can be used satisfactorily for a second run. On the other hand, in the reduction of many substances, the catalyst does not coagulate, but after the reduction is complete it gradually settles if allowed to stand, and the supernatant liquid may be decanted; when a second run is made with this catalyst it is frequently not much inferior to new catalyst and forms a fine suspension as soon as shaking is again started.

10. There is always a certain amount of the oxide which adheres to the filter paper during filtration, so that these papers should be ignited and the residue added to any platinum catalyst which has already become inactive and requires redissolving and reprecipitation (Note 3).

11. The thin film of oxide which remains in the casserole is dissolved by treating with a little constant-boiling hydrobromic acid (Note 8); the solution obtained may then be evaporated and the residue added

to the next fusion mixture.

12. In certain reductions it is an advantage to reduce the [platinum oxide](#) to platinum black by shaking with [hydrogen](#) in the presence of solvent only, before the substance to be reduced is added to the mixture. More often the catalyst is reduced in the presence of the substance to be reduced; with aldehydes, for example, the platinum black is usually more finely divided and generally more active if prepared in presence of the aldehyde.

13. Certain inorganic salts promote or retard the action of the catalyst.⁷ Thus, in the reduction of aldehydes, iron salts in mere traces have a remarkable effect in increasing the rate of reduction and in inhibiting the tendency of the catalyst to lose its activity. To a lesser extent [manganese](#), [nickel](#), and other salts have the same effect. On the other hand, with the majority of substances studied, these salts retard the reduction.

14. The solvent used is an important factor influencing the rate of reduction,⁷ and no generalization can be made beyond the one that [alcohol](#), either 95 per cent or absolute, has proved to be the best solvent for most of the compounds thus far studied. [Ethyl acetate](#) and glacial [acetic acid](#) may be used to advantage in some cases.

15. [Palladous oxide](#),⁸ PdO, may be prepared by the fusion of [palladous chloride](#) with [sodium nitrate](#); it is an effective catalyst in hydrogenation, the most active form being produced when the fusion temperature is 600°.

3. Discussion

[Platinic oxide](#) can be prepared by the interaction of [platinic chloride](#) and excess [sodium hydroxide](#),⁹ and by the fusion of chloroplatinic acid with [sodium nitrate](#).¹⁰ The catalyst itself is platinum black, and this can be prepared by the reduction of chloroplatinic acid with [formaldehyde](#),¹¹ the details for which have been improved by Willstätter and Hatt,¹² Willstätter and Waldschmidt-Leitz,¹³ and Feulgen,¹⁴ and by the reduction of [platinum oxide](#) with [hydrogen](#).¹⁰ A [platinum](#) catalyst can also be prepared from platinum black by heating with [oxygen](#) under pressure.¹⁵ Colloidal [platinum](#) or [palladium](#) catalysts, reported to be particularly valuable for the reduction of nitriles, oximes, and nitrostyrenes to amines, have also been described.¹⁶

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 61](#)
- [Org. Syn. Coll. Vol. 1, 101](#)
- [Org. Syn. Coll. Vol. 1, 240](#)
- [Org. Syn. Coll. Vol. 2, 489](#)
- [Org. Syn. Coll. Vol. 3, 501](#)
- [Org. Syn. Coll. Vol. 3, 685](#)
- [Org. Syn. Coll. Vol. 5, 567](#)

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

oxides of nitrogen

chloroplatinic acid

platinum black

platinum oxide-platinum black

Palladous oxide-palladium black

aminophenols

cyclic amino alcohols

bromoplatinic acid

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ethyl acetate (141-78-6)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

nitric acid (7697-37-2)

HYDROBROMIC ACID (10035-10-6)

bromine (7726-95-6)

oxygen (7782-44-7)

sodium nitrite (7632-00-0)

stannous chloride

platinum oxide,
Platinic oxide

Benzalacetophenone (94-41-7)

Benzylacetophenone (1083-30-3)

platinum (7440-06-4)

benzaldehyde (100-52-7)

zinc (7440-66-6)

palladium (7440-05-3)

sodium nitrate

ammonium chloroplatinate

potassium nitrate (7757-79-1)

manganese, nickel

Palladous oxide

palladous chloride (7647-10-1)

platinic chloride

Ethyl p-aminobenzoate (94-09-7)

ethyl p-nitrobenzoate (99-77-4)