2. *p*-Toluene-sulfonyl chloride does not react with *p*-mercury ditolyl under the above conditions.
3. *p*-Toluene-sulfonyl chloride and benzene-sulfonyl chloride react with *p*-mercury ditolyl at higher temperatures in toluene or xylene but give no more than traces of definite organic products.
4. No phenylmercuric chloride is obtained from the action of benzene-sulfonyl chloride and *p*-mercury ditolyl.

EVANSTON, ILLINOIS

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

PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. II. REDUCTION OF ALDEHYDES. ACTIVATION OF THE CATALYST BY THE SALTS OF CERTAIN METALS[1]

BY WALLACE H. CAROTHERS WITH ROGER ADAMS[2]

Received February 23, 1923

Introduction

In a previous article by Voorhees and Adams[3] it was shown that a very active catalyst for use in hydrogenation of all types of organic compounds was produced by the fusion of chloroplatinic acid with sodium nitrate. The behavior of the catalyst in the reduction of aldehydes was particularly commendable in that it permitted the reduction of comparatively large amounts of material with relatively small amounts of platinum in a brief period of time and since the publication of the preliminary article, this catalyst has been used for reducing large amounts of various aldehydes to the corresponding alcohols. These results were especially gratifying in view of the fact that aldehydes, in spite of the ease with which they are reduced to alcohols by ordinary chemical methods, have been found to be difficult to reduce by hydrogen using ordinary platinum black as a catalyst. This fact has been noticed by several investigators.[4]

A catalyst so easily prepared as this, which allowed such rapid reduction of all types of organic compounds, particularly of compounds so difficult to reduce catalytically as aldehydes, merited further study. The discovery of the cause for its very great superiority in many respects over

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[1] Part of the chloroplatinic acid used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.

[2] This communication is an abstract of a thesis submitted by W. H. Carothers in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Voorhees and Adams, THIS JOURNAL, **44,** 1397 (1922).

[4] G. Vavon, *Compt. rend.*, **154,** 359 (1912). This investigator found it possible to reduce aldehydes and ketones to alcohols but he recommends the use of 12 g. of platinum for each gram molecule of aldehyde.

other platinum catalysts might have a significant bearing on the theory of catalysis. In any event, the development of a general, satisfactory method of reduction for the preparation of various compounds by means of small amounts of platinum would be of considerable practical importance. The behavior of this catalyst in the reduction of aldehydes was studied first.

The preliminary experiments in this investigation were carried out according to the details outlined in the paper already referred to. Difficulty appeared immediately. Instead of reducing in the manner expected, about 10% of the theoretical amount of hydrogen was absorbed in a few minutes, and then the absorption fell off so rapidly that at the end of half an hour it had become very slow. The presence of an active poison toward the catalyst was at once suspected, but qualitative tests failed to reveal the presence of any common impurities. Moreover, the catalyst was found to behave normally toward pyridine and benzene rings, the reduction proceeding smoothly. Finally, careful purification of the chloroplatinic acid by three precipitations as the ammonium salt[5] failed to modify in the slightest degree the activity of the catalyst which was prepared from it. Since the chloroplatinic acid which was submitted to the purification just mentioned was purchased as a C. P. substance, it was necessary to conclude that the observed behavior was that of pure catalyst and that the catalyst used in the experiments described in the preliminary article had contained in small quantities some substance or substances other than platinum which caused the difference in activity. The catalyst used in these previous experiments was prepared from recovered platinum which had been worked over many times in forming platinum black according to the method of Feulgen.[6] The presence of impurities in it was not excluded, therefore; and since iron is an impurity which is likely to be present in platinum salts and also the one most likely to be introduced in laboratory operations, the effect of the addition of ferric chloride solution to the reaction mixture was tried.

The reaction which in the absence of ferric chloride had been almost infinitely slow, was now smoothly completed in 30 minutes, a most surprising result. This led us to make systematic experiments on the effect of various amounts of ferric chloride on the catalytic reduction of aldehydes. It soon became apparent that the ferric chloride was first being reduced to ferrous chloride, and that this latter substance was causing the activation. The majority of reduction experiments were, therefore, carried out with the addition of various amounts of ferrous chloride.

Pure benzaldehyde and heptaldehyde were chosen as representing typical

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[5] E. Wichers, THIS JOURNAL, **43**, 1268 (1921). See also Archibald, *Proc. Roy. Soc. Edinburgh*, **29**, 721 (1908-9).

[6] Feulgen, *Ber.*, **54**, 360 (1921).

aromatic and aliphatic aldehydes. Three series of experiments were completed. In each series only the concentration of the ferric or ferrous chloride was varied from one experiment to another.

Discussion of the Benzaldehyde Charts

Curve A (Fig. 1) represents the behavior of a benzaldehyde reduction using very pure catalyst and no ferric chloride. It will be observed that the rate of the reduction became practically zero within a very short period of time. When the reduction had completely stopped, the catalyst was re-activated by being shaken with air and the reduction then continued. After 4 such re-activations the absorption of the theoretical amount of hydrogen was completed.

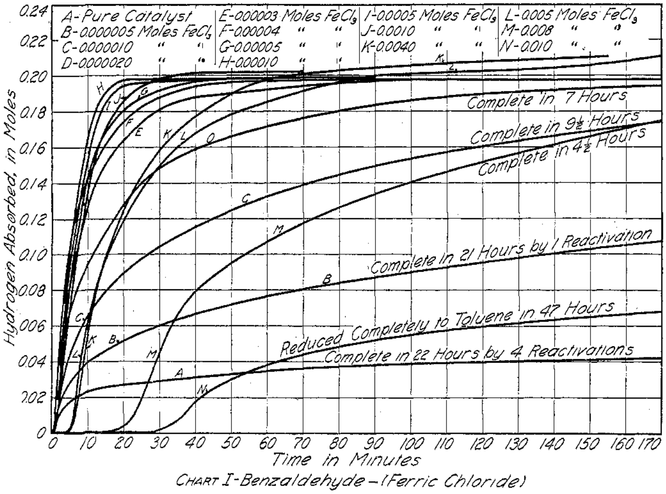

Fig. 1 (Chart I).—Series A. Benzaldehyde, 21.2 g. (0.2 mole); platinum oxide, 0.23 g. (0.001 gram atom of platinum); alcohol (95%), 50 cc.; ferric chloride solution containing from 0.000005 to 0.01 mole. For amounts greater than 0.0005 mole, proper volumes of aqueous 4 *M* ferric chloride solution were used; for amounts less than 0.0005 mole, proper volumes of 0.1 *M* ferric chloride solution were used.

All the other curves represent experiments in which various amounts of ferric chloride were added. To produce an appreciable change in the velocity of the reduction only very small amounts were required. Curve **B** is the curve for the experiment in which 0.000005 mole of ferric chloride was used. This was the smallest amount of ferric chloride employed, and since the volume of the solution in each experiment was about 70 cc. it corresponds to a concentration of only 4 parts of iron in a million parts of solution. Nevertheless, at the end of 25 minutes the reaction had proceeded as far in the presence of this low concentration of ferric chloride as it had in several hours in its absence. With increasing amounts of ferric chloride the speed of the reduction rapidly increased until the amount added corresponded to 0.0001 mole, and then with further increases the speed fell off until with 0.01 mole it became very slow. This last amount of ferric chloride corresponds to 10 moles of ferric salt to every atom of the platinum present. This decrease in speed with the comparatively concentrated ferric chloride was due to the gradual increase in the concentration of the hydrogen chloride present, formed by the reduction of the ferric chloride. No such change in the speed of the reductions was noted with high concentrations of ferrous chloride.

The greater amounts of ferric chloride gave a considerable induction period which lengthened as the amount of this salt was increased. This was interpreted to mean that, before the reduction of the aldehyde can begin, the ferric salt is reduced to the ferrous state. The correctness of this interpretation was indicated by experiments in which a phenolic aldehyde such as salicyl aldehyde or vanillin was used. The addition of ferric chloride to the reaction mixture containing such compounds produced immediately an intense purple color. With low concentrations of ferric chloride, this vanished within 1 minute when the mixture was shaken with the catalyst in the presence of hydrogen, thus indicating a conversion of ferric chloride to ferrous chloride. Until this color had completely disappeared, no measurable absorption of hydrogen took place. In accordance with this interpretation, the length of the induction period was found to be roughly proportional to the amount of ferric chloride present; with ferrous chloride it was very short and independent of the concentration.

The induction period is not entirely absent when no iron salt is present. The cause of this is to be studied in more detail. As was stated in the earlier paper, the induction period represents the time during which the yellow or brown platinum oxide is being transformed to the platinum black. Various samples of the catalyst differed somewhat in the time required for this reduction. It appeared to be autocatalytic; that is, only a trace of active platinum was present in the oxide, but this caused the reduction of the remainder to the active form, so that when the reaction started it at once became very rapid. Usually the induction period was not longer than 3 minutes in the absence of iron salt or in the presence of small amounts of iron salt, and with the sample used in most of the above experiments it was not longer than 1 minute. No definite evidence is available as to whether the ferric chloride or the platinum oxide was reduced first in the experiments in Fig. 1, but it would seem more probable that the platinum oxide was first reduced.

To eliminate the possibility of any difference in the experiments due to the varying induction periods of individual samples, the catalyst used throughout a series of experiments was taken from one large sample which was made by thoroughly mixing the products of several fusions. The pure benzaldehyde was prepared in one experiment.

Another effect of the use of high concentrations of ferric chloride was that the reduction did not stop sharply when the theoretical amount of hydrogen required for the formation of the alcohol had been absorbed, but instead proceeded beyond this point without inflection. In one experiment (Curve N, Fig. 1) in which the reduction was permitted to proceed beyond this point, the absorption became more rapid after somewhat more than the amount of hydrogen corresponding to the formation of the alcohol had been absorbed, and ultimately an amount of hydrogen was absorbed corresponding to complete reduction to toluene. At this point the reduction was interrupted although hydrogen was still being taken up at a regular rate. Toluene was the only substance isolated from the product, the yield amounting to about 60%.

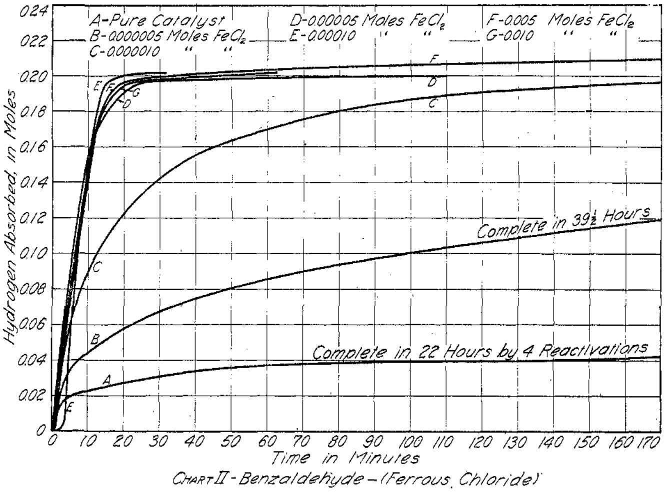

Fig. 2 (Chart II).—Series B. Same as Series A except that ferrous chloride solution containing from 0.000005 to 0.01 mole was used in place of ferric chloride.

For amounts greater than 0.0005 mole the proper volumes of aqueous 4.1 *M* ferrous chloride solution were used; for amounts less than 0.0005 mole proper volumes of 0.1 *M* ferrous chloride solution were used.

This phenomenon was ascribed to the effect of hydrogen chloride set free by the reduction of the ferric chloride, which might react with the benzyl alcohol to form benzyl chloride; the latter would be much more readily reduced than the alcohol. The detection of the unmistakable odor of benzyl chloride from many of the reaction mixtures when the more concentrated ferric chloride solutions were used, supported this possibility. It is, however, a curious fact that somewhat the same effect, although to a less degree, was observed when high concentrations of ferrous chloride were used, with which the concentration of the hydrogen chloride must have been exceedingly small.

When ferrous chloride (Fig. 2) was used instead of ferric chloride, the results were quite similar in the presence of small amounts of the salt. As before, the optimum amount of ferrous chloride for the particular volume used was 0.0001 mole. The results with larger amounts of ferrous chloride were, however, quite different from those obtained by the use of the corresponding amount of ferric chloride. The induction period was absent. Moreover, the rate of reduction was scarcely affected further by higher concentrations of ferrous chloride. Practically the only effect of such high concentrations was to increase slightly the time required for the reduction of the last traces of the aldehyde.

It is obvious that ferrous chloride is the reagent to use in place of ferric chloride in activating the reduction of aldehydes with platinum black, since with the former reagent no hydrogen chloride is formed which might either decrease the speed of the main reaction or cause other side reactions to take place.

Discussion of the Heptaldehyde Experiments

Similar results to those in the benzaldehyde experiments were obtained in the reduction of heptaldehyde (Fig. 3). The speed of reduction was enormously increased by the addition of ferrous chloride. Only by repeated

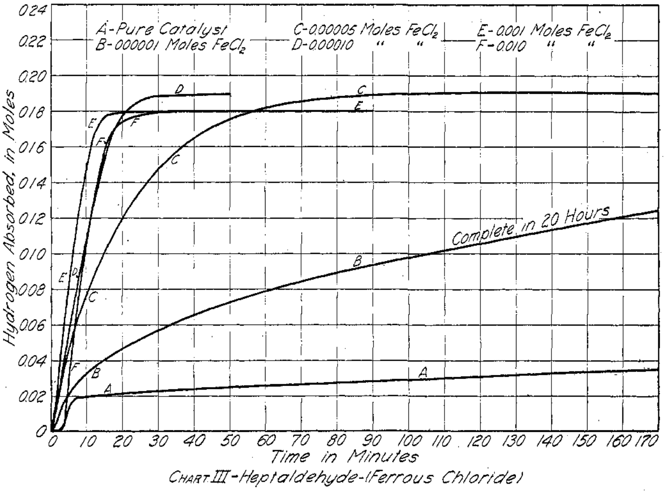

Fig. 3 (Chart III).—Series C. Heptaldehyde, 22.8 g. (0.2 mole); platinum oxide, 0.23 g. (0.001 gram atom of platinum); alcohol (95%), 65 cc.; water, 40 cc.; ferrous chloride solution containing from 0.00005 to 0.01 mole. For amounts greater than 0.0005 mole, the proper volumes of aqueous 4.1 *M* ferrous chloride solution were used; for amounts less than 0.0005 mole, proper volumes of 0.1 *M* ferrous chloride solution were used.

activation of the catalyst was it possible to reduce heptaldehyde with platinum black in the absence of the ferrous chloride.

Dil. alcohol was used as a solvent for heptaldehyde, since it was found that on adding even very small amounts of ferrous chloride to solutions of heptaldehyde in 95% alcohol, heat was evolved and in the reduction the absorption of hydrogen stopped at about 80% of that calculated. This was ascribed to acetal formation of polymerization, since it is well known that many salts catalyze these reaction;[7] the amount of heptaldehyde in each experiment, however, was too small to allow the isolation of such substances from the reaction mixtures. The use of 70% alcohol diminished this effect but did not eliminate it entirely, the absorption of hydrogen varying from 90 to 95% of the calculated amount. The experiments with heptaldehyde and benzaldehyde in which equal molecular quantities of ferrous chloride were used were, therefore, not comparable. It may readily be seen, however, that the degree of activation in both sets of experiments (Figs. 2 and 3) is approximately of the same magnitude.

In one or two preliminary experiments on the reduction of heptaldehyde, ferric chloride was employed in place of ferrous chloride. Uniformly successful results, however, were not obtained, since the hydrogen chloride set free apparently caused considerable polymerization and formation of acetal. Moreover, it was noted that the platinum in these experiments tended to precipitate and not stay suspended as when ferrous chloride was used, or as noticed in all of the benzaldehyde experiments.

Theoretical Discussion

Activation.—A number of investigators have noticed the difficulty in the catalytic reduction of aldehydes with platinum and palladium black. The explanation of this phenomenon is quite simple in terms of the theories and experimental results of Willstätter.[8] Oxygen is absolutely necessary for the activity of the catalyst. Benzaldehyde, being a readily oxidizable substance, robs the catalyst of its oxygen and makes it inactive. The effect of the ferrous salt is then specifically to inhibit the reaction, $PtO_2 + 2C_6H_5CHO \longrightarrow Pt + 2C_6H_5COOH$.

As previously stated, ferric salts are quite ineffective in promoting the catalysis until they have been reduced to the ferrous state, and this, together with the other facts described, makes it possible to relate the effect of the ferrous salt to negative catalysis.[9] Negative catalysts have often

[7] Adkins and Nissen, THIS JOURNAL, **44,** 2749 (1922).

[8] Willstätter and Waldschmidt-Leitz, *Ber.*, **54,** 113–8 (1921).

[9] In a recent article by N. R. Dhar and N. N. Mittra [*Chem. News*, **123,** 313 (1921)] an interesting general review of induced reactions and negative catalysis is given, and numerous examples are cited. Dhar concludes that in negative catalysis in oxidation reactions, a complex is formed of the two substances which are being oxidized and that this complex is then oxidized as a whole.

been called anti-catalysts; where oxidation is involved, the anti-catalysts have been called by Moureu[10] "antioxygènes" and by Lumière and Seyewetz[11] "antioxydants." All the known anti-oxidizers are substances likely to be oxidized themselves and are sometimes readily oxidized.

In this catalytic work the action which inhibits the catalytic reduction of the aldehyde is presumably the oxidation of the aldehyde by the platinum oxide in the platinum black. This latter reaction is a rapid one and renders the platinum black inactive within a very short time. Ferrous chloride is presumably also oxidized by platinum oxide, but probably only very slowly in the absence of any considerable quantity of hydrogen chloride. When added to the mixture of aldehyde and active platinum catalyst, the ferrous chloride acts as a powerful anti-oxidizer toward the oxidation of the aldehyde. The oxygen in the platinum is thus only very slowly removed and the catalyst, therefore, remains active toward the reduction of the aldehydes. The probability that this increased activity in the reduction of the aldehyde by the platinum is due to anti-catalysis by the ferrous chloride is strengthened by the study of the effect of the salts of certain other metals upon the catalytic reduction. Experiments with nickel and manganese chlorides in concentrations equivalent to the lowest concentration of ferrous salts which had a maximum efficiency showed that these salts have a similar though less pronounced action. The nickel is more effective than the manganese in aiding the catalytic reductions. Both of these salts exist in two states of oxidation like the iron salts and therefore might be expected to act as anti-catalysts. On the other hand, barium chloride or hydrogen chloride in molecular equivalent concentrations does not increase the activity of the platinum catalyst. It is probable that the salts of titanium, chromium and other metals, as well as certain organic compounds, will be found to act like ferrous chloride, and it is quite conceivable that some may be even more effective. The relative value of the various salts, oxides or hydroxides of iron has not yet been determined.

Other Effects of the Addition of Ferrous Chloride.—In the preliminary paper it was mentioned that as the platinum oxide was reduced, the platinum black which formed became distributed in a fine suspension throughout the alcohol solution. The addition of ferrous chloride apparently helps the platinum black to remain suspended, and the reduction is probably aided somewhat on this account. Moreover, the platinum black did not settle as readily after the reduction had been accomplished; it was never possible to allow the reaction mixture to stand and decant the solution. The platinum black, however, could be readily filtered with suction on asbestos in an atmosphere of carbon dioxide, and in this

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[10] Moureu and Dufraisse, *Compt. rend.*, **174**, 258 (1922); **175**, 127 (1922). See also Seyewetz and Sisley, *Bull. soc. chim.*, [4] **31**, 672 (1922).

[11] Lumière and Seyewetz, *Bull. soc. chim.* [3] **33**, 444 (1905).

way the platinum black was readily removed and a clear solution was obtained.

Willstätter[12] describes the coagulated form of the black as quite characteristic of oxygen-free, inactive catalyst; and fine subdivision and suspension as characteristic of active (oxygen-containing) platinum. If the oxygen content is actually the cause for the difference in subdivision, the explanation for the effect of the ferrous chloride in promoting the suspension is obvious—such platinum retains its oxygen more completely in the presence of the ferrous salt.

In order to show the gradual fatigue of the catalyst even in the presence of ferrous chloride and its recovery when shaken with air, 5.25 g. of benzaldehyde was dissolved in 50 cc. of alcohol and ferrous chloride added in an amount (0.05 cc. of 4 *M* solution) which could be diluted many times without decreasing its concentration below that which had the maximum effect on the catalyst. At this point, 0.06 g. of platinum catalyst was added. As soon as the 5.25 g. of aldehyde was completely reduced, another 5.25 g. in the same amount of alcohol was added and reduced; five such additions were made and reduced in succession without reactivation of the catalyst with air. The first portion was reduced in 8 minutes, the second in 21 minutes, the third in 65 minutes, the fourth in 215 minutes, and the fifth in about 10 hours. A sixth portion was finally added, but the solution was agitated with air for 5 minutes before the reduction was started. This sample was reduced in 12 minutes.

Experiments Indicating the Practicability and Economy of the Use of Ferrous Chloride in the Reduction of Aldehydes.—For the practical application of the use of ferrous chloride in the reduction of aldehydes with platinum black, it is obvious that the reduction can be most conveniently and rapidly carried out by adding the proper proportion of ferrous chloride to the mixture of alcohol, aldehyde and platinum oxide, allowing the reduction to continue until the speed of reduction begins to decrease, and then agitating the mixture with air; as soon as the speed again decreases, another reactivation is effected and this procedure continued to complete reduction. In this way a rapid reduction of a large amount of aldehyde can be carried out in a short period of time. In an experiment with 0.20 g. of catalyst, 50 g. of benzaldehyde, 130 cc. of alcohol and 2 cc. of 0.1 *M* ferrous chloride solution, the reduction was complete in 85 minutes. When a second portion of 50 g. of benzaldehyde was added and the mixture agitated with air for 5 minutes, the reduction was complete in 80 minutes. Thus it may be seen that with even the small amount of catalyst mentioned, 100 g. of aldehyde can be completely hydrogenated in considerably less than 3 hours.

In a second experiment with 0.025 g. of catalyst, 50 g. of benzaldehyde, 100 cc. of alcohol and 2 cc. of 0.1 *M* ferrous chloride solution, reduction

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[12] Ref. 8, p. 122.

took place to the extent of about 30% (on the basis of hydrogen required by calculation) during the first hour. At this point the reaction mixture was agitated with air for 5 minutes before the reduction was allowed to proceed. About 30% more hydrogen was thus absorbed in practically the same time as was required by the first 30%. The reaction mixture was again agitated with air and another 30% of the hydrogen was absorbed in about an hour. Finally, after another agitation with air, the last 10% was absorbed in 1 hour.

Effect of Change of Amount of Platinum Black on the Speed of Reduction. (Fig. 4.)—Experiments on the effect of various amounts of catalyst upon the speed of reduction of a standard amount of benzaldehyde gave results showing the high activity of this platinum–oxide platinum black. In Fig. 4 the results of four such experiments are shown in which all factors remained constant except the amount of catalyst. It is remarkable how rapidly such an extremely small amount of platinum catalyst will cause the reduction of benzaldehyde to take place, providing ferrous chloride is present. In each of the experiments, 21.2 g. of benzaldehyde was dissolved in 50 cc. of alcohol, and 1 cc. of aqueous 0.1 *M* ferrous chloride was added. When 0.23 g. of platinum oxide catalyst was used, the reduction was complete in 23 minutes, with 0.115 g. in 34 minutes, with 0.0575 g. in 60 minutes, and with 0.0288 g. in 5.5 hours. The catalyst in each of these experiments was taken from a single sample.

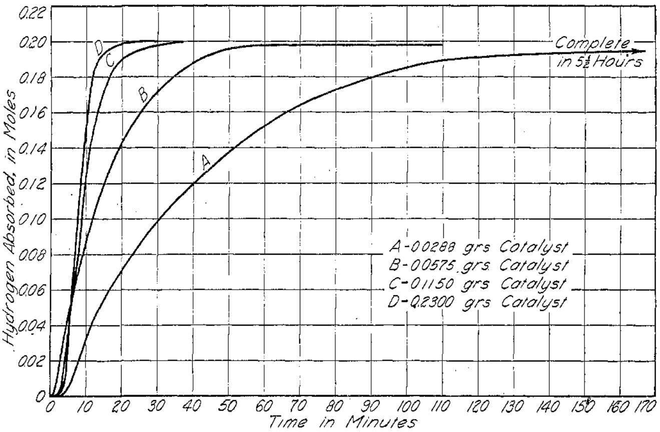

CHART IV-Benzaldehyde with Varying Amounts of Catalyst
Presence of 0.0001 Mole $FeCl_2$

Fig. 4.

Activity of Reworked Catalyst.—It was observed in the early experiments of the present investigation that platinum oxide from recovered chloroplatinic acid was often more active than the platinum oxide from which the recovered chloroplatinic acid had been formed. Occasionally, small traces of iron could be detected in such samples, but in other cases qualitative tests for iron were negative.

In view of the activation by accidental impurities of the catalyst described in the preliminary paper, and of the marked effect which extremely small quantities of iron salt have on the rate of the reduction, it became of interest to discover whether such impurities could accumulate in sufficient amounts to affect the rate of reduction when the operations involved in recovering the platinum from the catalyst were carried out with great care.

Starting with 1 g. of platinum oxide prepared from very pure chloroplatinic acid, 0.23 g. was weighed out and used in the reduction of 21.2 g. of benzaldehyde according to the directions already described. At the end of 6.5 hours, 0.026 mole of hydrogen had been absorbed. The reduction was then interrupted and the rest of the 1g. sample added and reduced to platinum black. The bottle was then opened and the black filtered off in an atmosphere of nitrogen through carefully washed asbestos. The platinum black was dissolved with aqua regia on the filter, evaporated with hydrochloric acid and then with water. The solution of chloroplatinic acid thus obtained was fused with sodium nitrate in the usual manner to prepare the oxide. In all this work especial care was taken to use pure reagents and to guard against the introduction of dust, etc. Of the catalyst prepared in this way, 0.23 g. was used in a second reduction of 21.2 g. of benzaldehyde, the details being identical with those of the previous experiment. At the end of 6.5 hours 0.040 mole of hydrogen had been introduced. A second recovery and reprecipitation of the oxide gave a sample which caused the absorption of 0.053 mole of hydrogen in 6.5 hours. The activity of the third sample of catalyst is not comparable with that produced by the addition of 0.00001 mole of ferrous chloride; it is, nevertheless, indisputable and significant.

Information was given us by a member of the staff of the United States Bureau of Standards who has had extensive experience in the analysis of C. P. chloroplatinic acid of both foreign and domestic production, that the impurities, and especially the iron content of such samples, varied from traces up to several per cent. This fact and the experiments described above which indicate the ease with which activating impurities can enter the platinum catalyst, lead to the question: To what extent have the results of previous investigators been influenced by the presence of small traces of foreign materials in the platinum used?

Possibilities for the Extension of the Addition of Foreign Substances to Platinum Black in Catalytic Reduction Experiments.—The present investigation has been limited to aldehydes on the one hand and, with the exception of a few experiments, to iron salts on the other, but it is anticipated that the method here outlined will, when extended to other types of organic compounds, yield results of much importance in hydrogenation. The obvious nature of the cause of the acceleration of the reduction of aldehydes by ferrous salts, leads to the expectation that the hydrogenation of other readily oxidizable organic compounds such as pyrrole derivatives may be accelerated in the same way. Moreover, it seems possible that in the reduction of α,β unsaturated aldehydes the addition of anti-catalysts will permit control of the point of initial reduction in the molecule.

In the case of the reduction of other substances not easily oxidized, the gradual decrease in the speed of reaction is presumably due chiefly to the gradual elimination of the oxygen in the platinum material by the hydrogen. Willstätter[13] has shown that platinum black that is absolutely oxygen-free and totally inactive may be prepared by shaking ordinary platinum black in suspension with hydrogen for 30 hours. It is reasonable to believe that ferrous salts or certain other substances will be found to act as anti-catalysts toward this reaction, under which conditions the active life of the platinum black would extend over a longer period of time than is usually observed, and thus increase the speed of reduction. The procedure described in this communication would then be general in its application. An experiment which supports this prediction is represented by Curve N on Fig. 1, where 0.01 mole of ferric chloride was used and the reduction continued for 47 hours. The aldehyde was completely reduced to alcohol at the end of 31 hours but the reduction continued and the toluene, at the end of 47 hours, was still steadily undergoing further reduction. It seems unlikely that the reduction would have continued readily after so long a period as 47 hours if the iron salt were not preventing the removal of the oxygen from the platinum material.

Various investigations have been made on the effect of foreign substances on the rate of catalysis by platinum metals, but of these only one is particularly pertinent to the present investigation. While this manuscript was being prepared, an article appeared by M. Faillehin[14] in which he calls attention to the difficulty of reducing aldehydes by the catalytic method, and states that when 5% of ferric chloride is added to the chloroplatinic acid used for the preparation of platinum black by a formaldehyde reduction, a catalyst more active toward aldehydes and ketones is produced. Using this catalyst he reduced piperonyl-4-butanone to the corresponding alcohol.

Experimental Part

Purification of Reagents

Platinum Oxide Catalyst.—The platinum oxide used in all of the experiments described in this communication was made from absolutely pure chloroplatinic acid.

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[13] Ref. 8, p. 124.

[14] Faillehin, *Compt. rend.*, **175**, 1077 (1922).

Ordinary C. P. chloroplatinic acid was precipitated thrice as the ammonium salt, according to the directions of E. Wichers.[5] Catalyst prepared from chloroplatinic acid purified in this way did not differ in catalytic activity from catalyst furnished by the Bureau of Standards which was certified as spectroscopically pure. The directions used for converting the chloroplatinic acid to the platinum oxide were the same as those described in the preliminary paper. Particular care was taken to use very pure sodium nitrate. One slight modification was made, however, which avoided the occasional tendency in certain of the experiments for the platinum oxide to be finely divided and difficult to filter. After the fusion was practically complete and no more nitrogen oxide fumes were evolved, the material was held in a molten state for 5 to 10 minutes at perhaps a slightly higher temperature than was necessary for the actual fusion. The material was treated with water, thoroughly washed, filtered and dried in a desiccator. The amount of chloroplatinic acid which was converted at one time varied from 1 to 5 g. The different samples of platinum oxide obtained were mixed so that a homogeneous sample was produced.

When the directions for the preparation of the catalyst are carefully followed, the yield is 85% of the calculated amount. It is preferable to prepare small lots (1 to 3 g.) since the precipitation of larger quantities requires a comparatively long time and the yields are sometimes lower. If it is found, after filtering off the platinum oxide, that the precipitation is incomplete the filtrates containing the sodium nitrate should be evaporated and fused again, when the greater portion of the remaining platinum will be precipitated in the form of oxide suitable for use as catalyst.

Benzaldehyde.—The benzaldehyde was purified by washing a C. P. grade of benzaldehyde twice with dil. sodium carbonate solution and then with water. After the aqueous layer had been separated as thoroughly as possible, the benzaldehyde was dried over anhydrous calcium chloride, filtered through glass wool and distilled under a diminished pressure of nitrogen into a Brühl receiver. The distillate was collected in 25g. portions in tubes with constricted necks. These were immediately sealed. Aldehyde was thus obtained which showed a benzoic acid content, by titration with dil. alkali, of less than 0.10%.

Heptaldehyde.—The heptaldehyde was purified by converting it first to the sodium bisulfite compound, which was thoroughly washed with alcohol and ether, dried and then treated with dil. sodium hydroxide containing less than the calculated amount of alkali necessary to neutralize all of the bisulfite. After the mixture had been heated with a current of steam, the layer of heptaldehyde floating on the surface was removed, washed and distilled under diminished pressure of nitrogen. The purified heptaldehyde was collected in exactly the same way as was the benzaldehyde and showed an acid content of less than 0.20%.

Ferric Chloride.—The ferric chloride solution was made by dissolving C. P. ferric chloride crystals in water and then diluting the solution to a known volume. Its concentration was determined by analysis.

Ferrous Chloride.—The ferrous chloride solution was produced by treating C. P. ferric chloride with acid-cleaned card teeth and C. P. conc. hydrochloric acid until it was completely reduced. After reduction the mixture was filtered and fresh card teeth added to the filtrate. This solution, with the card teeth still present, was evaporated to dryness under diminished pressure in an atmosphere of carbon dioxide, boiled distilled water was added and the solution again evaporated completely to dryness. The ferrous chloride crystals were then re-dissolved in boiled distilled water, filtered rapidly from the iron card teeth and placed in a bottle filled with carbon dioxide. The solution thus obtained was titrated and found to contain only traces of ferric chloride. It was analyzed for iron by oxidation and precipitation of the hydroxide so that its concentration was accurately known. This method was suggested by Dr. J. H. Reedy.

Procedure in Reduction Experiments.—The apparatus was practically the same as described in the preliminary paper except that a thermostat was placed around the hydrogen tank so that the temperature remained constant during all of the reductions. The tank was calibrated by measuring the volumes of hydrogen which corresponded to various pressure changes, and the gage readings were converted by calculation to moles. The actual readings on the course of the various reductions are not included in this paper because of lack of space. The reductions may be readily followed, however, by referring to the charts which were prepared from these data.

The initial pressure was in every case approximately 2.3 atmospheres. During the introduction of 0.2 mole of hydrogen the pressure dropped to 1.7 atmospheres. When more than 0.2 mole of hydrogen was needed, or the catalyst re-activated, the pressure was always restored to 2.3 atmospheres before resuming the reduction.

Readings were made at intervals varying with the rate of the reduction, but so fixed that an absorption of not more than 0.02 mole took place between every two readings. Usually the intervals were much smaller than this.

In the actual experiments, the aldehyde was removed from one of the tubes, weighed carefully, dissolved in alcohol and the platinum oxide catalyst and ferric or ferrous chloride solution then added. The bottle was evacuated, hydrogen admitted and the agitation commenced. The absorption of the gas was read in pounds pressure and then converted to moles of hydrogen.

Most of the reaction mixtures from the reductions illustrated in Fig. 1 and from all of the reductions of Fig. 2 were worked up separately in the following way. The reaction mixture was filtered through asbestos by suction in an atmosphere of carbon dioxide or nitrogen in order to remove the platinum black. The filtrate was then fractionated under diminished pressure with a good column. The benzyl alcohol was redistilled at atmospheric pressure and its weight determined. The yields were practically quantitative until the concentration of the ferric chloride was 0.001 mole, when the odor of benzyl chloride and toluene could be detected in the reaction mixture and the yield of benzyl alcohol began to decrease. With further increase in the ferric chloride, less benzyl alcohol was obtained and more toluene until in the experiment with the most concentrated solution, which was run until twice the calculated amount of hydrogen had been absorbed, only toluene was obtained although not in quantitative yield. About 60% of the calculated amount was isolated.

The materials used in the experiments on the reduction of heptaldehyde (Fig. 3) were worked up as follows. The platinum was filtered on asbestos in an atmosphere of carbon dioxide. The solution was saturated with potassium carbonate, the upper layer removed, dried with sodium sulfate and fractionated under ordinary pressure. The yields of heptyl alcohol were 16 to 20 g. or 70 to 90%.

All of the reductions were carried out at room temperature and no constant temperature bath or other controlling device was used. When the reactions were rapid, the mixtures spontaneously warmed to several degrees above room temperature. It was obvious that a variation in temperature had little effect since experiments could be accurately duplicated without considering the temperature in any way.

Revivification of Platinum.—The method used for the revivification of the catalyst in those experiments where it was carried out, consisted merely in withdrawal of the hydrogen by a vacuum pump, refilling the bottle with air and shaking it for 5 minutes. The air was then again removed and the hydrogen admitted.

Summary

1. Platinum black from platinum oxide prepared from absolutely pure chloroplatinic acid becomes very quickly inactive when shaken with an aldehyde in an atmosphere of hydrogen; only by frequent re-activation can the reduction be carried to completion.

2. The addition of as much as 4 parts per million of iron in the form of ferrous or ferric chloride greatly accelerates the rate of the reduction.

3. A systematic study has been made of the effects of various amounts of ferrous and ferric chloride on the catalytic reduction of benzaldehyde, and of ferrous chloride on the catalytic reduction of heptaldehyde, using the platinum oxide catalyst described in a previous paper. In all cases an optimum effect is observed when the amount of iron chloride present corresponds to a concentration of approximately 0.0001 mole in 100 cc. of the reaction mixture.

4. When higher concentrations of ferrous chloride are used the only additional effect observed is a very slight diminution in the rate of reduction and a tendency for the reduction to proceed beyond the alcohol stage.

5. When ferric chloride is used it is first reduced to ferrous chloride. With amounts of ferric chloride not greater than 0.0001 mole the effect is quite similar to that produced by ferrous chloride. With larger amounts an induction period appears and the reduction becomes slower because of the hydrogen chloride set free in the reduction of the ferric chloride. The reduction proceeds beyond the formation of benzyl alcohol to toluene and even further.

6. It is shown that foreign materials sufficient to increase the activity of the catalyst appreciably are accumulated during its recovery even when C. P. reagents are used and every precaution is taken to guard against the entrance of accidental impurity.

7. Evidence is given for the following interpretation of the effect of the ferrous salt. The inactivity of the pure platinum black is due to the fact that it is deprived of the oxygen necessary for its activity by the readily oxidizable aldehyde. The iron salt specifically inhibits this reaction and so prolongs the active life of the catalyst.

8. Using appropriate amounts of ferrous chloride and 0.23 g. of catalyst, it is shown that 21.2 g. of benzaldehyde may be smoothly reduced to the alcohol in 20 to 25 minutes. The reaction then stops and no further reduction takes place. A method is described for reducing 100 g. of benzaldehyde in 4 hours with 0.025 g. of catalyst.

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NOTES

The Action of the Grignard Reagent on Keto Acids.—The action of the Grignard reagent on esters of γ-keto acids, where but 1 molecular proportion of the Grignard reagent is used to 1 of the ester, has been known for some time. This reaction involves the addition of the Grignard reagent to the keto group, which on hydrolysis of the reaction product gives a lactone of the hydroxy acid. Various yields have been reported depending on the type of reacting substances. In certain cases where the keto acid is difficult to prepare, or to esterify, it is desirable to use the Grignard reagent on the keto acid directly, thus eliminating not only the necessity of preparing the ester but also the probable loss of valuable material. In connection with other work which has led to the preparation of *iso*-campholactone from 3-keto-1,2-dimethyl-cyclopentane-carboxylic acid, the reaction of the Grignard reagent on levulinic acid was first studied.

*iso*Caprolactone was prepared by the action of methylmagnesium iodide on levulinic acid. Methyl magnesium iodide was slowly added to an ether solution of levulinic acid in the proportion of 2 moles of the former to 1 mole of the latter. On the addition of the first half of the Grignard reagent, an insoluble magnesium salt of levulinic acid was formed; but after the addition of the remainder, a slow reaction took place which continued for 4 hours, giving a second insoluble compound. After the reaction mixture had been cooled the addition compound was decomposed by 1:1 sulfuric acid and the *iso*caprolactone extracted with ether. The ether extract was washed with a solution of sodium bisulfite to remove free iodine. After the ether had been distilled, the residue was fractionated, and that portion boiling at 205–210° under atmospheric pressure was saved; yield, 31.5%. Noyes and Marvel[1] obtained a yield of 30–35% from ethyl levulinate.

The lactone of γ-methyl-γ-hydroxy-hexanoic acid was prepared in a similar manner by the action of 2 molecular proportions of ethyl magnesium

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[1] Noyes and Marvel, This Journal, **39**, 1269 (1917).