A comparison of the cupric and picrate-picric reduction methods in these determinations of "reserve" polysaccharides is given in Table II.

These results would indicate that no advantage is offered in the hydrolysis of this class of material by increasing the percentage of hydrochloric acid over 0.5%, for there is clearly a destruction of glucose even with 1% hydrochloric acid.

Summary

A colorimetric method for the determination of starch by means of conversion with taka-diastase without a secondary hydrolysis has been described. Under the conditions of conversion, the ratio of glucose to maltose is remarkably constant and the analytical error introduced by regarding this ratio as 2.0 is very small, since the picrate-picric reducing ratio of glucose to maltose is relatively high. A method also for the determination of other "reserve" polysaccharides has been given.

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

PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. V. THE PREPARATION OF PRIMARY ALCOHOLS BY THE CATALYTIC HYDROGENATION OF ALDEHYDES[1]

BY WALLACE H. CAROTHERS[2] WITH ROGER ADAMS

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In a previous paper,[3] the writers have described the results of a study of the behavior of the platinum oxide catalyst of Voorhees and Adams[4] in the hydrogenation of benzaldehyde and heptaldehyde. It was shown that these aldehydes are only slowly and very incompletely reduced when certain impurities are rigorously excluded from the aldehyde and the catalyst, but that in the presence of small amounts of iron salts, the reduction is rapid and complete. The study has now been extended to include, on the one hand, the effect of a large number of substances on the rate of hydrogenation of benzaldehyde and, on the other hand, the effect of ferrous chloride on the catalytic hydrogenation of a variety of aldehydes and some other types of compounds. In this communication are described the re-

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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 part 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] Carothers with Adams, THIS JOURNAL, **45**, 1072 (1923).

[4] (a) Voorhees with Adams, *ibid.*, **44**, 1397 (1922). See also (b) Adams and Shriner, *ibid.*, **45**, 2172 (1923); and (c) Kaufmann and Adams, *ibid.*, **45**, 3029 (1923).

sults obtained in the reduction of several aldehydes under various conditions.

Many aldehydes are much more readily available than the corresponding alcohols, and hence methods for the reduction of aldehydes are of considerable value in synthetic work. Of all such methods a satisfactory catalytic method is, in many respects, the most desirable. The possibilities of the use of the catalytic method for the preparation of alcohols have, of course, been examined by previous investigators, and in particular by Vavon,[5] who reduced a large number of aldehydes using platinum black as a catalyst. He emphasized the advantages of this method—quantitative yields, simplicity of isolation of products, etc. The directions of Vavon, however, call for an amount of platinum equal to 10% of the weight of the aldehyde to be reduced, and hence this method must be regarded as unsatisfactory for general use. The discovery of the promoting effect of iron salts made by the writers[3] makes possible the use of a very much smaller amount of platinum (less than 0.1% of the weight of the aldehyde to be reduced), and the considerations set forth above have made a restudy of the catalytic method for the preparation of alcohols desirable.

It may be stated at once that the behavior of pure catalyst toward a variety of aldehydes is similar to its behavior toward benzaldehyde, and it seems probable that the lack of catalytic activity is characteristic of pure platinum black toward pure aldehydes in general; moreover, that of the large number of substances examined as possible promoters, none is more powerful nor more generally satisfactory than ferrous chloride. All the experiments to be described later were, therefore, (except where otherwise specified) carried out in the presence of 0.1 millimole of ferrous chloride; and attention was devoted to such other conditions as might influence the rate of the reduction and the ease of isolation of the alcohols

[5] Vavon, *Compt. rend.*, (a) **154,** 359 (1912); (b) *Ann. chim.*, 1, 144 (1914).

It may be of some interest to compare the results presented in this paper with those obtained by previous investigators. Vavon reduced a large number of aromatic aldehydes. He recommends the use of 10 to 12 g. of platinum black for 1 g.-mole of aldehyde. The reduction is complete in a few hours.

Skita [(c) *Ber.*, **42,** 1627 (1909); (d) **45,** 3312 (1912); (e) **48,** 1486 (1915)]; (f) Skita and Meyer, [*Ber.*, **45,** 3589 (1912)] and (g) Skita and Ritter [*Ber.*, **43,** 3393 (1910)] reduced several aldehydes using colloidal palladium or colloidal platinum.

Ipatiew [(h) *Ber.*, **45,** 3218 (1912)] reduced a few aldehydes using high pressure and either palladium black or nickel as a catalyst; for example, 30 g. of citral was reduced almost completely to decanol in the presence of 1 g. of palladium black at 110° under a hydrogen pressure of 110 atmospheres in 6 to 7 hours.

Sabatier and Senderens [(i) *Compt. rend.*, **137,** 301 (1904)] have shown that their method using a nickel catalyst is very satisfactory for the reduction of lower aliphatic aldehydes to alcohols.

Aldehydes have also been reduced by v. Braun and Kochendörfer, [(j) *Ber.*, **56,** 2172 (1923)] using hydrogen at 25 atmospheres and nickel salts as catalysts; 100 g. of benzaldehyde was reduced to the alcohol in one hour at 140–150°.

produced. In these experiments the following procedure (referred to as the standard procedure) was deviated from only in the instances specified.

Two-tenths mole of the aldehyde is dissolved in a suitable volume of a solvent, 0.5 cc. of 0.2 *M* ferrous chloride solution and 0.1725 g. of the platinum oxide catalyst[4b] is added, the bottle[6] is attached to the shaker, connected with the hydrogen tank and evacuated until the solvent boils, hydrogen is admitted at three atmospheres (total pressure), and as soon as thermal equilibrium has been established, the shaker is started. Shaking is continued until the change in pressure indicates the absorption of the calculated amount of hydrogen, or until no more hydrogen is absorbed. The bottle is then removed and the platinum filtered off with suction on an asbestos pad on a Gooch plate set at the bottom of a tall, cylindrical separatory funnel, the pad being always kept covered with liquid to prevent air coming in contact with the platinum black on the asbestos. The solvent is removed from the filtrate by distillation under diminished pressure.

In all these experiments, the catalyst used was prepared from chloroplatinic acid which had been very carefully purified by the method previously described and which was, therefore, quite free from all metals except platinum, since only in this way was it possible to be certain that no unknown variables were affecting the results. Catalyst from C. P. chloroplatinic acid, and catalyst from purified chloroplatinic acid have been found, however, to give practically identical results in experiments of the kind here described (namely, in the presence of ferrous chloride) so that for practical purposes, the purification of the platinum would be unnecessary.

Effect of Solvent

In the experiments previously described, 95% ethyl alcohol was used as a solvent, because considerable experience in this Laboratory in the hydrogenation of a large number of types of compounds had shown it to be generally satisfactory. It is known, however, that the nature of the solvent may have a very considerable effect on the rate of hydrogenation reactions, and the behavior of a number of solvents was therefore examined.

Experiments were first made to determine the rate of the reduction in the absence of solvents and in various dilutions of ethyl alcohol. The times should be compared with the time, 25 minutes, required in the standard procedure for benzaldehyde [0.2 mole (21.2 g.)] using 50 cc. of 95% ethyl alcohol as a solvent.

Using benzaldehyde without a solvent, the absorption of hydrogen was very slow. At the end of 100 minutes, only 70% of the calculated amount

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[6] The apparatus used is that described by Voorhees and Adams, Ref. 4 a.

had been absorbed and at the end of 260 minutes, 92%. At the end of the reaction, part of the platinum was found plated out on the sides of the bottle, and the rest had become colloidal so that it could not be filtered off. Heptaldehyde behaved similarly under like conditions.

When 25 cc. of 95% ethyl alcohol was used as solvent, the reduction of benzaldehyde was complete in about 70 minutes, with 50 cc. in 25 minutes, and with 100 cc. in 20 minutes.

The following solvents were tested in the reduction of benzaldehyde (using 100 cc. of solvent): acetone, glacial acetic acid, ethyl acetate, petroleum ether, absolute ethyl ether, pyridine and benzene. The relative velocities of the reduction in these solvents decreased in the same order as they are written. In the last four, the reduction was extremely slow, being far from complete at the end of four hours. In acetone the calculated amount of hydrogen for reduction to the alcohol was absorbed in 15 minutes, and further absorption of hydrogen occurred without any break in the reaction-velocity curve with hydrogenation of the acetone. This, however, did not occasion any difficulty in the isolation of the product. With glacial acetic acid, the reduction was complete in about 45 minutes, and in ethyl acetate, in about 160 minutes.

Unfortunately, the effect of the solvent appears to be to some extent specific. The reduction of heptaldehyde which in 60% alcohol required 40 minutes, in ethyl acetate required 210 minutes, and in acetone, 270 minutes. The reduction of vanillin required 60 minutes in 95% alcohol and 150 minutes in acetone. For piperonal the times in 95% ethyl alcohol and glacial acetic acid were 15 and 80 minutes, respectively, while in acetone the reduction was only 65% complete in 142 minutes and in ethyl acetate 90% complete in 170 minutes. The order given for benzaldehyde cannot, therefore, be generalized, but ethyl alcohol appears to be the best solvent in most cases.

The possibility of the existence of undesirable secondary effects due to the promoter and the catalyst and the possibility of considerably modifying the properties of the solvent by the addition of small amounts of substances other than these is illustrated in experiments in which methyl alcohol was used as a solvent.

When 100 cc. of technical methyl alcohol was used in the reduction of benzaldehyde, some evolution of heat occurred on the addition of the ferrous chloride. The initial part of the reduction was quite rapid, 60% of the calculated amount of hydrogen being absorbed in five minutes. The reaction then became very slow and practically stopped when it lacked 30% of being complete. Unchanged benzaldehyde was then absent from the liquid as shown by a negative test with phenylhydrazine under conditions which permitted the detection of very small amounts of benzaldehyde in the presence of considerable benzyl and ethyl alcohols; but the peculiar odor of acetal was present, and after being warmed with a drop of concd. hydrochloric acid the mixture gave, when treated with phenylhydrazine, a copious precipitate of benzaldehyde-phenylhydrazone. It was concluded that the incompleteness of the reaction was due to the formation of the dimethyl acetal of benzaldehyde. Titration of the methyl alcohol used as solvent indicated that it was about 0.0004 *N* with respect to acid. When 100 cc. of perfectly neutral absolute methyl alcohol was used as solvent, the behavior was similar but the reaction was 94% complete before it stopped; that is, here there was acetal formation to the extent of 6% and in the previous experiment, to the extent of 30%. Finally, methyl alcohol was used which had been distilled from sodium. The calculated amount of hydrogen was with this solvent absorbed in about 10 minutes. When this methyl alcohol was titrated it was found to be 0.0034 *N* with respect to sodium methylate, and similar velocities could be obtained using 100 cc. of technical methyl alcohol to which 0.00034 mole of sodium hydroxide or sodium methylate had been added. Description of a number of experiments which were made in this connection will be omitted for the sake of brevity, but it may be mentioned that it appears that the hydrogen-ion concentration must be kept very low, since even small amounts of acid cause the formation of considerable amounts of acetal, and that the presence of free alkali is undesirable since it causes the precipitation of the iron hydroxide that covers the surface of the catalyst and so diminishes its activity.

The behavior of absolute ethyl alcohol as a solvent is precisely similar to that of 95% ethyl alcohol so far as the initial velocity of the reduction of benzaldehyde is concerned. The reaction tends, however, to proceed further, the benzyl alcohol being slowly reduced to toluene. Little or no acetal formation is observed. When sodium ethylate is added to the absolute ethyl alcohol, the initial velocity of reduction is considerably increased, but the behavior is not always consistent, and magnification of the induction period and difficulty in the reduction of the last few per cent. of the aldehyde sometimes appear. These deviations from the normal course of the reduction velocity curve are still more marked when sodium hydroxide is added. The effect of the addition of alkali may then be somewhat to decrease or somewhat to increase the total time required for the reduction. Whether alkali is to be added or not will be determined by the properties of the aldehyde to be reduced and the solvent used. With benzaldehyde in methyl alcohol, the addition of alkali avoids the formation of acetal; in ethyl alcohol no formation of acetal occurs, and so the use of alkali is unnecessary. With aliphatic aldehydes, acetal formation occurs even in ethyl alcohol, and so here the addition of alkali may be advisable.

There is still another function which small amounts of alkali may serve. Certain alcohols, notably phenolic alcohols, are very sensitive to the action of minute amounts of acid;[7] and since traces of acid are usually introduced with the ferrous chloride, the addition of alkali may be, if not necessary to prevent the complete polymerization of the product, at least desirable as an aid in its isolation. The use of alkali is, therefore, governed by the desire to obtain the best yield of the best material in the shortest time. In some cases it may suffice to add it after the reduction is complete; in others its use may be quite unnecessary.

Phenolic Aldehydes and the Aldehydes of Phenol Ethers

Salicylic Aldehyde.—The behavior of salicylic aldehyde in the presence of pure catalyst is similar to that of benzaldehyde. The following directions are very satisfactory in the preparation of saligenin[8] from salicylic aldehyde.

One hundred cc. of 95% ethyl alcohol is used as solvent for 27.2 g. of the aldehyde and the standard procedure followed. The red color which develops on addition of the platinum oxide vanishes on shaking with hydrogen in 40 seconds. The reduction is complete in one hour. Before the platinum is filtered off, 0.4 cc. of *N* aqueous sodium hydroxide is added. The residue from the distillation of the solvent is a mass of reddish crystals of saligenin. When crystallized from 150 cc. of hot benzene, 92% of the calculated amount of saligenin is obtained as large, flat, white, glittering crystals with a very faint pink tinge; m. p., 84.5–85°. By evaporation of the benzene mother liquors, the rest of the product is obtained as a mass of reddish crystals.

When sodium hydroxide is not added before the platinum is filtered off, the product is blue, the crystals are smaller and less pure (m. p., 81–2°), and the residue from the evaporation of the mother liquors is frequently a sticky solid.

Vanillin.—The behavior of vanillin in the presence of pure platinum oxide is similar to that of benzaldehyde.

The most satisfactory procedure for the reduction of vanillin is the standard one using 150 cc. of absolute alcohol as solvent and adding 0.36 millimole of sodium ethylate before adding the ferrous chloride. The reduction is complete in about one hour, and on crystallization from 200 cc. of benzene the vanillyl alcohol[9] is obtained as slightly pink crystals; m. p., 113–114°; yield, 94–96%. The results are the same when 95% alcohol is used as solvent, but the time required is somewhat longer—about 2 hours.

In some early work it was attempted to use ferric chloride as a promoter. The reduction was rapid, but when the solvent was distilled with the view to isolating the vanillyl alcohol, a viscous residue was obtained with an extremely sharp and choking odor (formaldehyde). As the residue was warmed on the steam-bath it turned brown in spots, and on cooling, the amorphous mass was found to be insoluble in all common solvents. It was suspected that the acid set free by the reduction of the ferric chloride was the cause of the polymerization,[7] but when ferrous chloride was used as a promoter and 95% alcohol as a solvent similar results were frequently obtained. The residue

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[7] The great sensitivity of phenolic alcohols toward acids has been commented on by (a) Tiemann, *Ber.*, **8**, 1124 (1875); (b) Manasse, *Ber.*, **27**, 2411 (1894); and (c) Lederer, *J. prakt. Chem.*, **50**, 224 (1894).

[8] Saligenin has been prepared from salicylic aldehyde (a) by reduction with sodium amalgam, Reinecke and Beilstein [*Ann.*, **128**, 179 (1863)] and by catalytic hydrogenation (Ref. 5a).

[9] Vanillyl alcohol has been prepared together with hydrovanilloin by the treatment of vanillin with sodium amalgam in the presence of aqueous alcohol [Tiemann, Ref. 7 a, p. 1125; *Ber.*, **9**, 415 (1876)]; and by the catalytic reduction of vanillin, (Ref. 5 a, p. 360).

from the distillation of the solvent was a blue liquid with a strong odor of formaldehyde, and although this liquid was soluble in benzene no crystals separated on evaporation. In a similar experiment using absolute ethyl alcohol as a solvent the reduction was complete in 50 minutes and then proceeded slowly beyond the theoretical limit (compare the behavior of benzaldehyde described above). As the residue (a blue liquid having a strong odor of formaldehyde) after distillation of the solvent was cooled, it gradually solidified, and on crystallization from benzene, 50% of the calculated amount of vanillyl alcohol was obtained as a blue powder; m. p., 112–113°. Apparently, a little sodium ethylate is necessary to avoid the polymerization completely. The addition of sodium hydroxide after the completion of the reduction as in the preparation of saligenin (instead of the addition of sodium ethylate at the start) results in a somewhat lowered yield of slightly less pure material, from which it would appear that the polymerization must to some extent occur during the course of the reduction.

Anisaldehyde.—Using the standard procedure (100 cc. of 95% ethyl alcohol as solvent) of 27.2 g. of anisaldehyde is reduced in 22 minutes, 0.4 cc. of *N* sodium hydroxide is added to the liquid before the platinum is filtered off, and the residue after removal of the solvent is distilled in a vacuum, yielding 25.2 g. (92%) of anisyl[10] alcohol; b. p., 127–130° at 8 mm. The distillation should be carried out rapidly and without the use of a column, since if a column is used the higher bath-temperature necessary induces a secondary reaction with the formation of a high-boiling fraction. If a column is used and the distillation is carried out very slowly, practically the entire product may consist of this fraction.

Piperonal.—Using 100 cc. of 95% alcohol as solvent, 30 g. of piperonal is reduced in 11 minutes. The residue from the distillation of the solvent crystallizes on cooling, and on crystallization from a mixture of ethyl ether and petroleum ether, piperonyl alcohol[11] separates as white crystals; m. p., 52–53°; yield, 27.5 g.

Halogen Derivatives of Benzaldehyde

No complications appear in the reduction of the halogen derivatives of benzaldehyde. No formation of acetal is observed in 95% alcohol. Titration of the filtrate from the reduction mixture indicates the absence of any considerable amount of halogen acid, from which it may be concluded that the halogen of the ring[12] is not appreciably affected under the conditions of these experiments. No difficulties appear in isolating the alcohols. Four-tenths cc. of *N* sodium hydroxide was usually added before filtering off the platinum.

p-Chlorobenzaldehyde.—p-Chlorobenzyl alcohol[13] was obtained as yellowish-white

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[10] Anisyl alcohol has been prepared by the electrolytic reduction of anisaldehyde [Tafel and Schepss, *Ber.*, **44,** 2148 (1911); Law, *J. Chem. Soc.*, **91,** 748 (1907)]; and by the catalytic reduction of anisaldehyde [Ref. 5 a, p. 360].

[11] Piperonyl alcohol has been prepared by the action of sodium amalgam on piperonal [Fittig and Remsen, *Ann.*, **159,** 138 (1871)] and by the catalytic reduction of piperonal [Ref. 5 a, p. 361].

[12] Halogen is removed from the ring with great ease under some circumstances. See, for example, Rosenmund and Zetzsche, *Ber.*, **51,** 578 (1918); Borsche and Heimbürger, *Ber.*, **48,** 452, 850 (1915); Busch and Stöve, *Ber.*, **49,** 1063 (1916); Kelber, *Ber.*, **50,** 305 (1917).

[13] p-Chlorobenzyl alcohol has been prepared by the electro-reduction of p-chlorobenzaldehyde [(a) Law, *J. Chem. Soc.*, **99,** 1114 (1911)].

needles from a mixture of benzene and ligroin in a yield of 92.4%; m. p., 71–72.5°. The time of reduction was 1 hour for 0.2 mole.

_p_-Bromobenzaldehyde.—_p_-Bromobenzyl alcohol was obtained in a yield of 96% as pure white crystals from a mixture of ethyl ether and petroleum ether; m. p., 76–76.5°. The time of reduction was 15 minutes for 0.1 mole.

_o_-Chlorobenzaldehyde.—_o_-Chlorobenzyl alcohol[14] was obtained in a yield of 96%; m. p., 64–65°. The time of reduction was 24 minutes for 0.2 mole.

Aliphatic Aldehydes

Heptaldehyde.—The reduction of heptaldehyde to heptyl alcohol[15] has already been described.[3] To diminish the formation of acetal instead of diluting the solvent with water, 0.3 millimole of sodium ethylate or sodium hydroxide may be added before the addition of the ferrous chloride.

Aldol.—From a commercial sample of aldol, 17.6 g. of pure material was obtained by distillation in a vacuum. When reduced using the standard procedure (with 50 cc. of 95% alcohol as solvent) about 93% of the calculated amount of hydrogen was absorbed in about two hours. The yield of butanediol-1,3,[16] b. p., 103–104° (8 mm.) was 86% of that calculated on the basis of the hydrogen absorbed.

Butyraldehyde.—Very little reduction occurred in the absence of iron salts. In the presence of 0.1 millimole of ferrous chloride (using ethyl alcohol as a solvent) the reduction was at first fairly rapid, but remained incomplete (due to acetal formation). When 0.3 millimole of _N_ sodium hydroxide solution was added before the ferrous chloride the reduction proceeded practically to completion in two hours.

Aldehydes not Reduced

One of the purposes of the experiments reported in this paper was to find the limitations of the method here described, that is, what aldehydes are not reduced. It may be said that none of the aldehydes tried have proved to be totally incapable of reduction by the methods here described. The sugar aldehydes (as represented by glucose) reduce with such extreme slowness as to make this method quite impracticable for the preparation of the corresponding alcohols. All other aldehydes tested were reduced without the expenditure of an unreasonable amount of time. Resorcylic aldehyde was reduced completely, although rather slowly, but from the reduction product only a black gum could be isolated. _p_-Di-

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[14] _o_-Chlorobenzyl alcohol has been prepared by the electro-reduction of _o_-chlorobenzaldehyde (Ref. 13 a, p. 1116).

[15] Heptyl alcohol has been prepared by the reduction of heptaldehyde (a) with zinc in acetic acid solution [Bouis and Carlet, _Ann._, **124**, 352 (1862); Krafft, _Ber._, **16**, 1723 (1883)]; (b) with sodium amalgam [Jourdan, _Ann._, **200**, 102 (1880); Cross, _Ann._, **189**, 2 (1877); Boeseken and v. Senden, _Rec. trav. chim._, **32**, 23, 37 (1913)]; (c) catalytically [Ref. 5 f, pp. 3591, 3593]; (d) electrolytically [Schepss, _Ber._, **46**, 2568 (1913)]; (e) with sodium and acetic acid in toluene [Levene and Taylor, _J. Biol. Chem._, **35**, 281 (1918)].

[16] Butanediol-1,3 has been prepared by (a) the action of sodium amalgam on acetaldehyde or acetaldol [Kekulé, _Ann._, **162**, 310 (1872); Würtz, _Bull. soc. chim._, [2] **41**, 362 (1884); Demjanoff, _Ber._, **28**, 22 (1895)]; (b) from acetaldehyde or acetaldol by the action of magnesium amalgam [Meunier, _Compt. rend._, **134**, 473 (1902); Kling and Roy, _ibid._, **144**, 1112 (1907); _Bull. soc. chim._, [4] **1**, 697 (1907)]; (c) from acetaldol or paraldol by the action of aluminum amalgam [Halpern, _Monatsh._, **22**, 63 (1901)]; (d) from acetaldehyde or aldol by electrolytic reduction [Perkin, _J. Soc. Chem. Ind._, **31**, 623 (1912)].

methylaminobenzaldehyde was reduced readily, but attempts to distil the reduction product resulted in the formation of a gum.

Aside from these cases the method here described appears to be quite general in its applicability.

Summary

The discovery made by the writers of the promoting effect of iron salts on the catalytic reduction of aldehydes using platinum black as a catalyst has been applied to a number of aldehydes with the view (1) to determining how general this effect is and (2) to working out a satisfactory general method for the reduction of aldehydes. A standard procedure is described, the advantages and limitations of this method are set forth, and detailed directions are presented for the preparation of various primary alcohols.

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

THE PREPARATION OF PALLADOUS OXIDE AND ITS USE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS.[1] VI

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In previous papers, a convenient method for the preparation of platinum dioxide and its successful use as a catalyst in the hydrogenation of organic compounds has been reported.[3] Since the method of preparing an oxide by fusion of chloroplatinic acid with sodium nitrate gave an excellent catalyst in the case of platinum, a study of the preparation of oxides from other noble metals by the same procedure has been undertaken. This communication reports on the preparation of palladous oxide and preliminary experiments on its use as a catalyst.

Palladium has been widely used as a reduction catalyst as palladium black and as a colloid[4] and, in many cases, appears superior to platinum. This investigation has been undertaken in the hope of finding a more active and conveniently prepared palladium catalyst than has been produced

[1] Part of the palladium 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 R. L. Shriner in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers and Adams, *ibid.*, **45**, 1071 (1923). (c) Adams and Shriner, *ibid.*, **45**, 2171 (1923). (d) Kaufmann and Adams, *ibid.*, **45**, 3029 (1923).

[4] For a good review of the use of palladium black and colloidal palladium, see "Catalysis in Organic Chemistry," by Sabatier, translated by E. E. Reid, D. Van Nostrand Co., 1922.