[Contribution from the Research Laboratories, School of Pharmacy, University of North Carolina]

Palladium Catalysts. VIII.[1] Catalysts Prepared in the Presence of Various Organic Anions

WILLIAM D. CASH,[2] FRED T. SEMENIUK, AND WALTER H. HARTUNG

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The effect of certain organic anions in the preparation of palladized charcoal was investigated. Catalysts were prepared by reducing ionic palladium in five organic acid–sodium salt buffer solutions and were studied in hydrogenations of nitrobenzene, quinone, piperonal oxime, benzaldehyde, benzyl alcohol, and propiophenone.

In reductions of nitrobenzene, quinone, and propiophenone, certain catalysts were more active than catalysts prepared in the absence of organic anions; others were less active. The most active catalyst in the reduction of one substrate was not necessarily the most effective in reducing another compound.

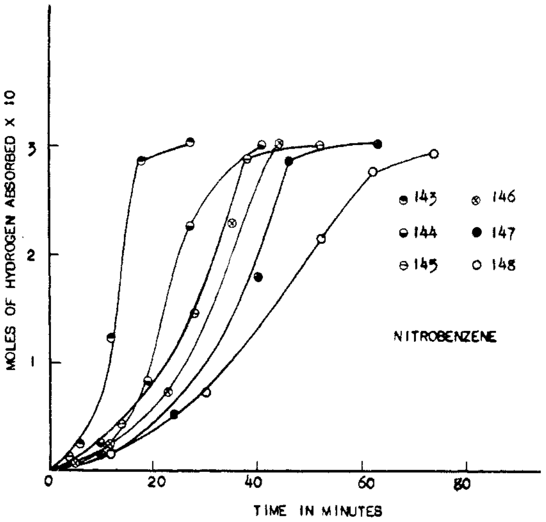
Benzaldehyde, benzyl alcohol, and piperonal oxime were reduced at about the same rate by all the catalysts.

The modifications in activity imparted by the organic anions are attributed to influences exerted by the anions in determining the crystalline structure or the spacing of active centers in the finished catalyst.

The activity of palladized charcoal in the catalytic hydrogenation of organic compounds can be altered to some extent by modifying the method by which the catalyst is prepared.[1,3–5] For example, a catalyst prepared by reducing ionic palladium in a charcoal suspension containing sodium acetate shows different properties from a catalyst prepared with the acetate absent.[6] These differences have prompted investigation into the effect produced by other organic anions in the catalyst preparation.

Groups of five catalysts were prepared by reducing identical amounts of palladous chloride in buffer solutions composed of the following anions: acetate, mandelate, succinate, lactate, and tartrate. A plain catalyst also was prepared with each group.[7] The catalysts were observed for differences in activity in reductions of nitrobenzene, quinone, piperonal oxime, benzaldehyde, benzyl alcohol, and propiophenone. Curves were plotted for each reduction, and representative experiments are summarized in the accompanying figures.

In the reductions of nitrobenzene, quinone, and propiophenone, significant variations in activity were observed among the catalysts within a group, *i.e.*, catalysts containing the same amount of palladium metal but prepared in the presence of different organic anions.[8] Mandelate and succinate catalysts were most active with nitrobenzene (Fig. 1). Succinate or no organic ion was most effective



Figs. 1–6.—Catalysts Prepared in the Presence of Different Organic Anions.

Fig. 1.—19 mg. of palladous chloride per gram of Nuchar. *143*—Mandelate; *144*—Succinate; *145*—Plain; *146*—Acetate; *147*—Lactate; *148*—Tartrate.

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(1) For No. VII see Young and Hartung, *J. Org. Chem.*, **18**, 1659 (1953).

(2) Fellow, American Foundation for Pharmaceutical Education, 1951–1954. Present address: Department of Biochemistry, Walter Reed Army Institute of Research, Washington 12, D. C.

(3) Young, Thesis, University of North Carolina, 1952.

(4) Hartung and co-workers, unpublished work.

(5) Young, Hartung, and Daniels, *J. Org. Chem.*, **18**, 229 (1953).

(6) See note 10, Hartung and Chang, *J. Am. Chem. Soc.*, **74**, 5927 (1952).

(7) The catalysts are named in terms of the anion used in their preparation. Thus, "acetate" means that acetic acid–sodium acetate buffer solution was employed. For the "plain" catalyst no organic anion was present.

(8) Earlier papers[1,5,6] mention that the activity of catalysts prepared under seemingly identical conditions may show poor reproducibility. Before undertaking the experiments described here, the question of reproducibility was investigated further. It appears that a modification in the preparation to obtain more uniform wetting of the charcoal with the solution of ionic palladium, thereby affording more uniform adsorption of the ions, leads to much better reproducibility.

Each of the substrates mentioned above, except benzyl alcohol, was reduced with four identical plain and four identical acetate (modified) catalysts. Only in the hydrogenations of quinone with the acetate catalysts and of propiophenone with the plain catalysts were there appreciable variations. These results seemed to justify the design of the experiments in this study.

Reductions of nitrobenzene and quinone (Figs. 1 and 2) were repeated with the most active catalysts. The same results were obtained.

It should be mentioned that the question of reproducibility is still not conclusively settled, although other workers in these laboratories also seem to have solved it at least in part.

with quinone (Fig. 2). With propiophenone the lactate, mandelate, and succinate catalysts were as active as the acetate catalyst and considerably more active than the tartrate and plain catalysts (Fig. 6).

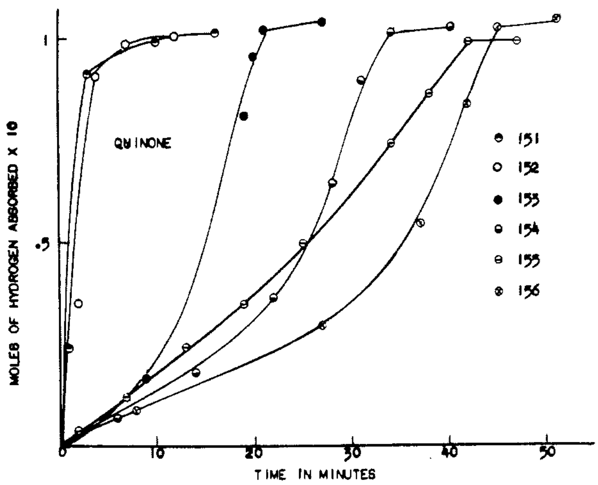


Fig. 2.—12 mg. of palladous chloride per gram of Nuchar. *151*—Plain; *152*—Succinate; *153*—Mandelate; *154*—Acetate; *155*—Tartrate; *156*—Lactate.

In reductions of benzaldehyde, benzyl alcohol, and piperonal oxime (Figs. 3–5) all six catalysts exhibited approximately equal activity. That is, the variations were no greater than observed among identical plain or identical acetate catalysts with these substrates.

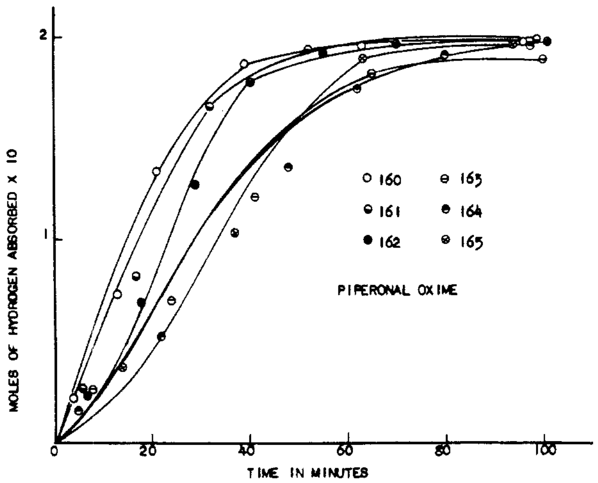


Fig. 3.—150 mg. of palladous chloride per gram of Nuchar. *160*—Mandelate; *161*—Lactate; *162*—Acetate; *163*—Succinate; *164*—Plain; *165*—Tartrate.

It is seen that the most active catalyst for one substrate may not be the most effective for another.

It was suspected that the characteristic activity of the acetate as compared to the plain catalyst might be attributed to the great difference in hydrogen ion concentration of the solution from which the metal is deposited on the carrier. It had been previously observed that palladium deposited from a solution, by passing hydrogen gas through it, is dense and has a metallic luster at pH 2 and is spongy and dull at pH 6. However, experiments reveal that the differences in catalytic activity cannot be explained entirely on the basis of change in

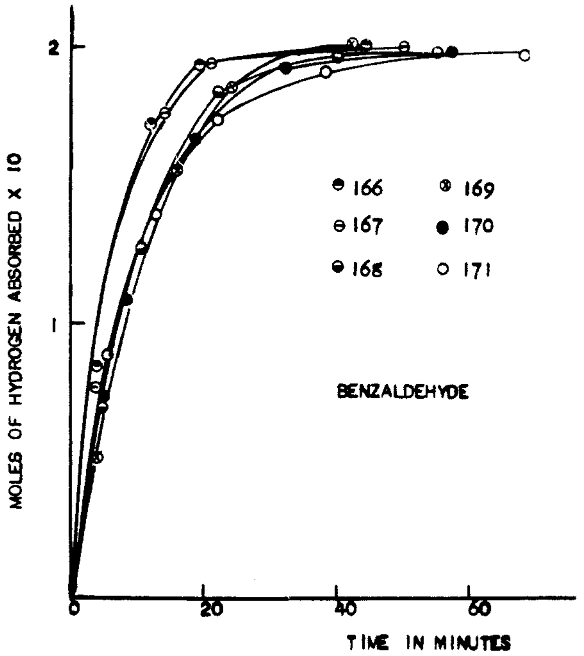


Fig. 4.—25 mg. of palladous chloride per gram of Nuchar. *166*—Succinate; *167*—Mandelate; *168*—Acetate; *169*—Lactate; *170*—Tartrate; *171*—Plain.

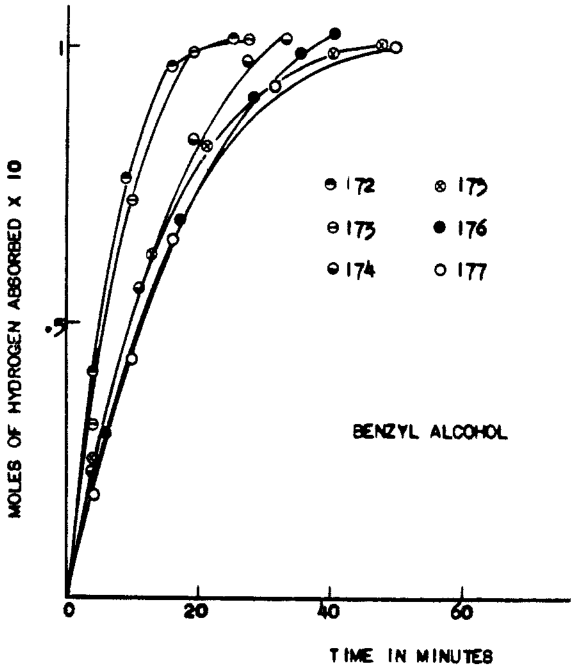


Fig. 5.—25 mg. of palladous chloride per gram of Nuchar. *172*—Plain; *173*—Mandelate; *174*—Lactate; *175*—Acetate; *176*—Tartrate; *177*—Succinate.

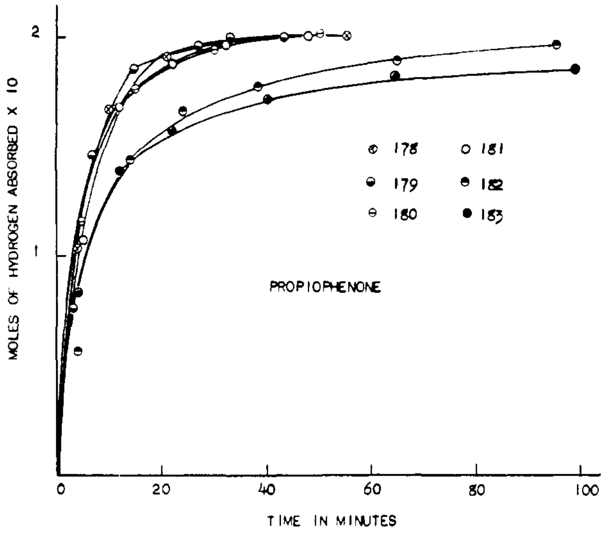


FIG. 6.—125 mg. of palladous chloride per gram of Nuchar. *178*—Acetate; *179*—Mandelate; *180*—Lactate; *181*—Succinate; *182*—Tartrate; *183*—Plain.

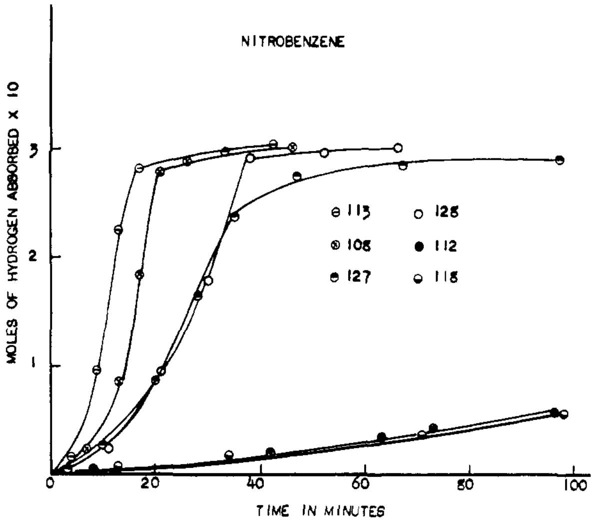
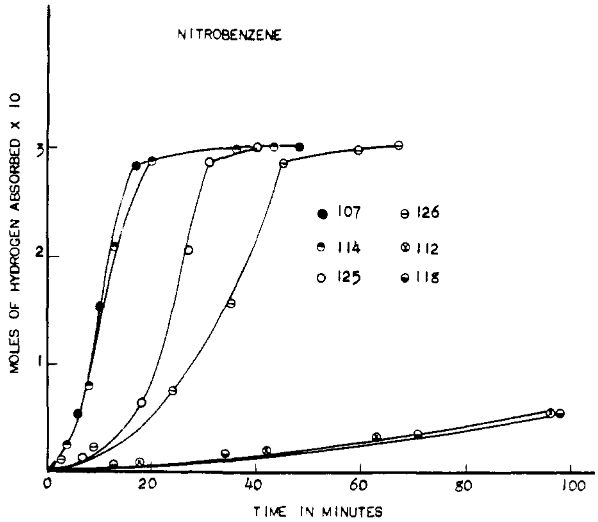


FIG. 8.—19 mg. of palladous chloride per gram of Nuchar. *113, 108*—Mandelate, *p*H 3.5–3.6; *127*—Mandelate, *p*H 2.7–2.8; *128*—Hydrogen Malonate, *p*H 3.6–3.7; *112, 118*—Hydrogen Malonate, *p*H 2.7–2.8.

*p*H. Figures 7 and 8 show this very well. However, it should be noted that the activities of catalysts prepared in the presence of the same ion do vary with change in *p*H.

A molar ratio of mandelate to palladium of 10:1 was sufficient to provide typical mandelate effect (Fig. 9). When the ratio was reduced to 3:1, the catalyst possessed greater activity toward nitrobenzene than did the plain catalyst. Experiments with the mandelate ion suggest that there may be an optimum stoichiometric relationship between the anion and the palladium cation.

The anion must be present when ionic palladium is adsorbed by the charcoal or during its reduction to metallic palladium. Typical mandelate effect was obtained by triturating the charcoal with palladiumchloride in mandelate buffer solution, then filtering off the charcoal with adsorbed ions, and reducing the adsorbed ionic palladium directly in the hydrogenation medium. This catalyst was more active than a plain catalyst similarly prepared from unbuffered solution (Fig. 10). Trituration of the charcoal first with mandelate buffer solution and then with palladium chloride solution did not give a typical mandelate catalyst. Nor was mandelate activity obtained by mixing a finished plain catalyst with mandelate buffer solution.



FIGS. 7, 8—CATALYSTS PREPARED AT DIFFERENT HYDROGEN ION CONCENTRATIONS.

FIG. 7.—19 mg. of palladous chloride per gram of Nuchar. *107, 114*—Malonate, *p*H 6.4–6.8; *125*—Acetate, *p*H 6.4–6.6; *126*—Plain, *p*H 2.1–2.4; *112, 118*—Hydrogen Malonate, *p*H 2.7–2.8.

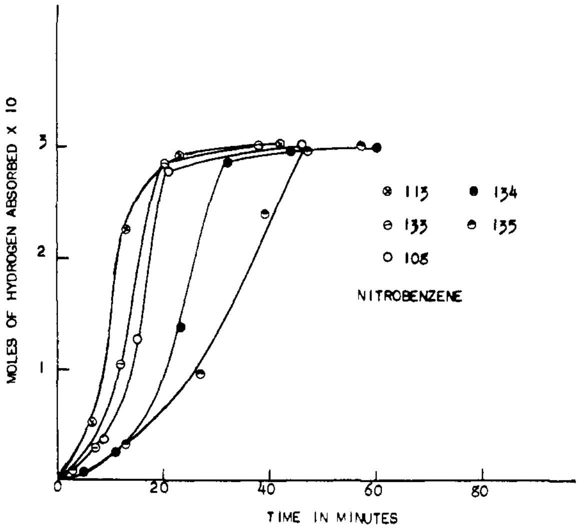


FIG. 9.—DILUTION EXPERIMENTS WITH MANDELATE BUFFER SOLUTION. 19 mg. of palladous chloride per gram of Nuchar. *113, 108*—0.002 *M* palladous chloride in 1 *M* mandelate; *133*—0.002 *M* palladous chloride in 0.02 *M* mandelate; *134*—0.002 *M* palladous chloride in 0.006 *M* mandelate; *135*—Plain.

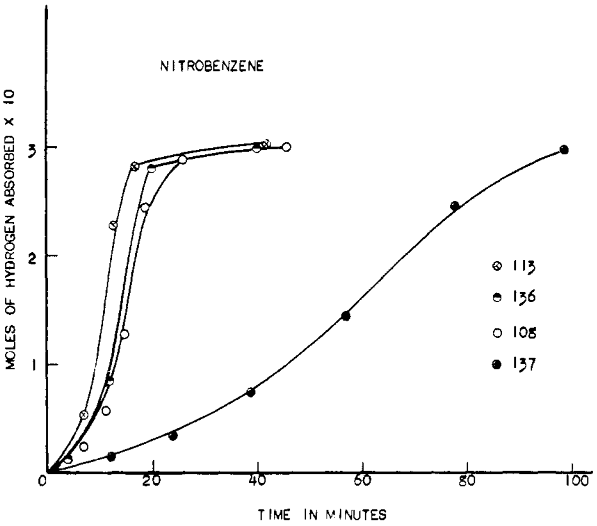


FIG. 10.—CATALYSTS CONSISTING OF NUCHAR WITH ADSORBED PALLADIUM IONS. 19 mg. of palladous chloride per gram of Nuchar. *108, 113*—Mandelate, prepared in usual manner; *136*—Nuchar was triturated with palladous and mandelate ions, the charcoal with unreduced adsorbed ions was dried, the palladous ion was reduced directly **in the** reduction medium; *137*—Catalyst prepared as *136* **except** in the absence of mandelate ions.

If, as these results appear to suggest, the palladium ion forms some combination with the anion, possibly a complex or a salt, it would conceivably afford a finished catalyst in which the crystalline structure or the spacing of the active centers is a function of the anion.

Lihl and Zemsch[9] have reported different initial activities for nickel catalysts prepared by reducing the formate, oxide, hydroxide, and oxalate. Piccard and Thomas[10] obtained a very active hydrogenation catalyst when ionic palladium was first precipitated from a solution of its chloride by the addition of sodium carbonate, then was redissolved in glacial acetic acid and reduced to metallic palladium.

EXPERIMENTAL

All reductions were carried out on a Parr apparatus. All substrates were carefully purified, and dried absolute ethyl alcohol was used as the solvent. Piperonal oxime was hydrogenated in 3 *N* ethanolic hydrogen chloride.

Since the reduction pathways and yields of product for all the substrates had been previously established,[3,4] the products were not isolated in these investigations. Quinone forms hydroquinone; benzaldehyde and propiophenone form the corresponding carbinols or toluene and propylbenzene, respectively; nitrobenzene yields aniline; benzyl alcohol, toluene; and piperonal oxime, in the presence of HCl, forms piperonylamine hydrochloride.

Palladium chloride was supplied gratuitously by the American Platinum Works. The sample was the purest available and contained the equivalent of 60 per cent free palladium.

Nuchar C-190 (practical) was used as the carrier for all catalysts.

Buffer solutions were prepared by dissolving one mole of the acid in enough distilled water to make about 1800 ml., adding sufficient sodium hydroxide to adjust the *pH* to the *pK* value, and diluting to 2000 ml. with distilled water.

In each catalyst preparation the desired volume of palladium chloride stock solution, containing 2.50 g. of $PdCl_2$ per 100 ml., was added to 100 ml. of the buffer system, or to 100 ml. of water in the preparation of plain catalysts. Nuchar (2 g.) was triturated in a glass mortar with about 25 ml. of the resulting solution. The thick suspension then was transferred to a reduction bottle, using the remaining solution for rinsing the contents of the mortar into the bottle. Reduction was carried out for 30 minutes at a pressure of approximately 60 p.s.i. The finished catalyst was filtered, washed thoroughly with distilled water, and dried overnight with the aid of phosphoric anhydride and reduced pressure.

In reductions of the substrates the directions for operation described by Adams and Voorhees[11] were followed generally.

CHAPEL HILL, NORTH CAROLINA

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[9] Lihl and Zemsch, *Z. Elektrochem.*, **56**, 979 (1952); [*Chem. Abstr.*, **47**, 5779 (1953)].

[10] Piccard and Thomas, *Helv. Chim. Acta*, **6**, 1044 (1923); [*Chem. Abstr.*, **18**, 778 (1924)].

[11] Adams and Voorhees, *Org. Syntheses*, Coll. Vol. 1, 2nd Ed., 63 (1941).