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

PALLADIUM CATALYSIS. VI.[1, 2] THE REPRODUCIBILITY OF PALLADIUM-ON-CHARCOAL CATALYSTS

JAMES G. YOUNG,[3] WALTER H. HARTUNG, AND H. H. DANIELS[4]

Received October 6, 1952

A study is under way in these laboratories to determine if possible the effects of difference in carrier, modifications in preparation, drying, aging and storing, ratio of palladium to carrier, ratio of palladium to promotor, and other factors on the catalytic reactions. It soon became apparent that before reliable data purporting to assay these variations may be evaluated, it is necessary to determine first to what degree catalysts which presumably are identical in every known detail duplicate each other with respect to rate and degree in hydrogenation reactions. This is a summary of experiments on reducing a few selected substrates under arbitrarily established but constant conditions.

In this study "divided" and "duplicate" catalysts were employed. The "divided" catalysts were prepared using four grams of carrier and before use divided into equal halves. The "duplicate" catalysts were prepared in single catalyst amounts of two grams each, and every known precaution was taken to allow no variation of any kind. The ratio of palladium to carrier was adjusted to what is called a "minimal" value, which was determined in preliminary trials as that ratio which suffices to produce hydrogenation over some convenient period of time, say 30 minutes to several hours. Generally, for synthetic purposes, the variations in time and extent of hydrogenation may be minimized by using larger amounts of palladium.

The results obtained with typical simple substrates (benzaldehyde, nitrobenzene, quinone and piperonal oxine) are described, and the data are given graphically.

It is evident from the results of this study that there was considerable variation in the activity of catalysts which were presumably identical and used under identical conditions. This variable activity is difficult to explain; perhaps it may be attributed to factors which could not be controlled under the experimental conditions employed.

The cause of the wide differences in catalysts designed to be identical is especially difficult to identify in the case of the "divided" catalysts. However, a plausible explanation for the duplicated catalysts is that in their formation, during which the palladium is deposited on the carrier from a solution of its ions, there is a random formation of "active centers", which may vary sig-

---

[1] For Number V see Y. T. Chang and W. H. Hartung, *J. Am. Chem. Soc.*, **75**, 89 (1953).

[2] Presented in part before the Division of Medicinal Chemistry at the 121st Meeting of the American Chemical Society, Milwaukee, Wis., March 30 to April 3, 1952.

[3] Fellow, American Foundation for Pharmaceutical Education, 1949–1951. Present address, Medical College of Virginia, Richmond.

[4] A grant from Sharp and Dohme to the North Carolina Pharmaceutical Research Foundation for assistance is gratefully acknowledged.

nificantly from one catalyst to another even though every precaution is taken to control all known factors. This random formation may manifest itself in a difference in the spacing of active centers, which according to the Langmuir concept (1) is the factor which determines the activity of a catalyst, or in variations in the crystalline lattice structures of deposited palladium atoms. H. S. Taylor (2) considers the latter to be the determining factor since such differences would affect the number of active centers and their ability to reduce any single substrate.

Support for this postulate of the random formation of active centers is seen in catalysts prepared with a carrier which may be dissolved away, *e.g.*, palladium-on-barium carbonate or palladium-on-magnesium oxide. It is true that the character of the catalytic reaction is modified by the use of another carrier, but by the use of a series of such presumably identical catalysts with, say, benzaldehyde as substrate, considerable variations were also observed; and when samples of the catalyst were placed on a microscope slide and the carrier dissolved away with acid, there remained the particles of palladium of varying sizes, and in general the catalyst yielding the greater number of larger particles gave slower hydrogenation. It is not presumed that the particles of palladium after removal of the carrier are identical with those deposited on the carrier, but they undoubtedly are a clue to the random difference in active centers.

The marked differences in the activity of the "divided" catalysts as compared to the "duplicate" catalysts, while unexpected, are not altogether unreasonable. Differences in the nature of the palladium on the carrier may be expected when in one instance palladium was deposited on four grams of carrier, while in the "duplicate" catalyst two grams of carrier were used. This matter deserves further attention.

Aside from theoretical considerations, the results of this study serve to emphasize the importance of accuracy and precision in catalytic hydrogenation experiments, and indeed, add impetus to the statement of Homer Adkins (3): "It may not be amiss, however, to suggest that the author of a paper upon catalytic hydrogenation should state exactly how he prepared his catalyst; how much of it and the hydrogen acceptor be used; at what pressure of hydrogen, at what temperature, and for how long the reaction was carried out; and how much of each product was actually isolated in a pure state."

EXPERIMENTAL

The *palladinized charcoal catalysts* were prepared according to the method of Reeve and Hartung (4) by shaking in hydrogen a mixture of palladous chloride solution and charcoal in 100 ml. of distilled water containing six grams of anhydrous sodium acetate; the catalyst was filtered off by suction, washed with distilled water, and dried *in vacuo* over phosphoric anhydride. Care was taken to use exact amounts of carrier and palladium and to dry the catalysts not less than 36 hours and not more than 48 hours.

The *carrier* was Nuchar obtained from Eastman Kodak Co. In an attempt to remove any gases which may have been sorbed, the carriers were heated in an oven at 100–110° for six to seven hours, cooled in a vacuum desiccator, and stored in tightly stoppered bottles. For each catalyst, 2.0 grams of carrier was used.

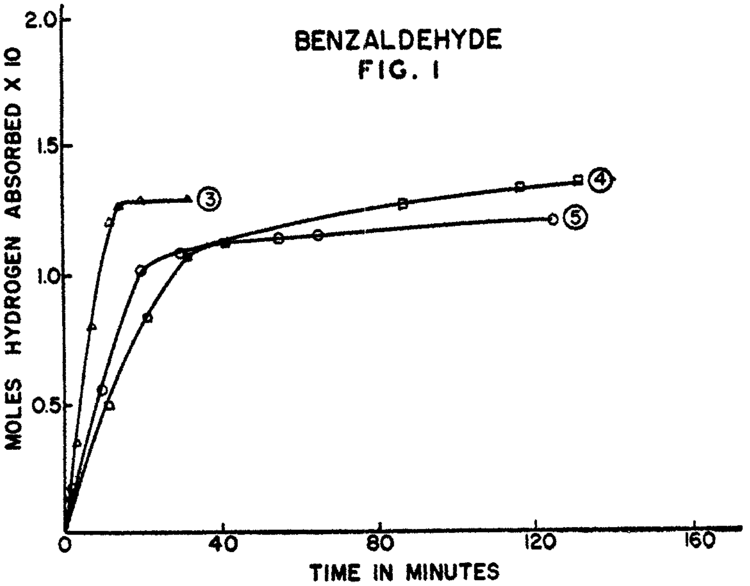

Fig. 1. Run 3—30 mg. of palladium on 2.0 grams of charcoal; runs 4, 5—60 mg. of palladium on 4.0 grams of charcoal—catalyst divided into equal halves.

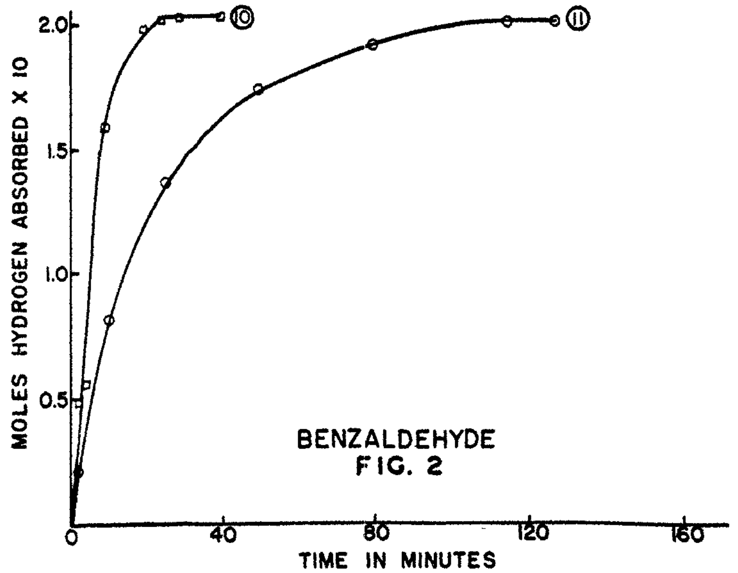

Fig. 2. Runs 10, 11—120 mg. of palladium on 4.0 grams of charcoal—catalyst divided into equal halves.

The *substrates* employed were benzaldehyde, nitrobenzene, quinone, and piperonal oxime. The liquid compounds, all C.P. products, were distilled, the first and last 10% of the distillates being discarded. Each of these compounds was then shaken with a palladi-

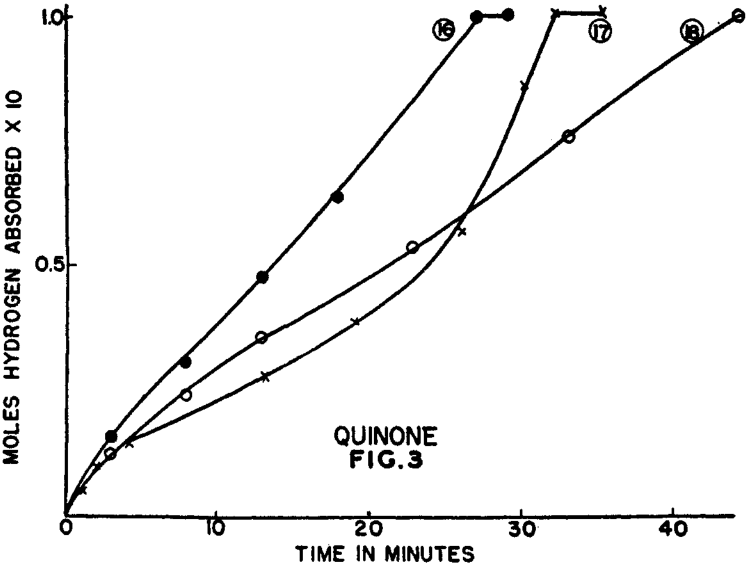

FIG. 3. Runs 16, 18—30 mg. of palladium on 4.0 grams of charcoal—catalyst divided into equal halves; run 17—15 mg. of palladium on 2.0 grams of charcoal.

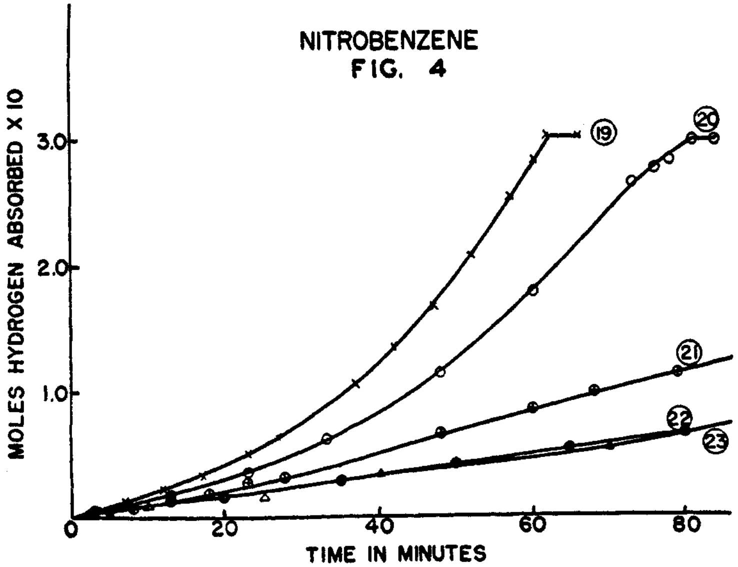

FIG. 4. Runs 19, 20, 23—"Duplicate" catalysts each containing 15 mg. of palladium on 2.0 grams of charcoal; runs 21, 22–30 mg. of palladium on 4.0 grams of charcoal—catalyst divided into equal halves.

nized charcoal catalyst for several hours and the catalyst filtered out. These operations were intended to remove likely impurities that might possibly "poison" the catalysts. The "detoxified" compounds were stored in tightly stoppered amber bottles until used.

The *quinone*, obtained from Eastman Kodak Co., was of "White Label" purity and was used without further purification.

The *piperonal oxime*, prepared according to the method of Shriner and Fuson (5), was purified by recrystallization from dilute alcohol.

The *reduction medium* in all cases was commercial absolute alcohol which had been refluxed with lime and distilled.

The apparatus employed was a Parr hydrogenator equipped with a pressure gauge and automatic shaking attachment.

All the reductions were started at room temperature under an initial hydrogen pressure of approximately 60 p.s.i.g. The directions for operation described by Adams, *et al.* (6) were followed in all cases.

In every reduction one-tenth mole of substrate was dissolved in 100 ml. of absolute alcohol.

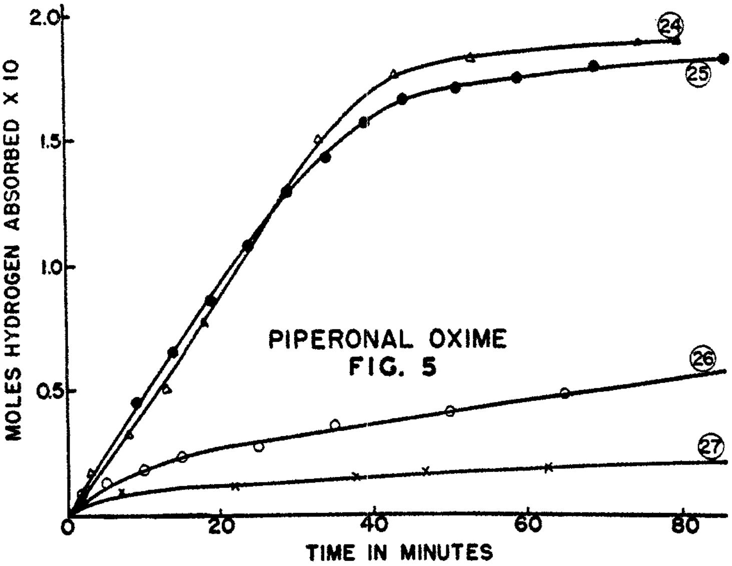

FIG. 5. Runs 24, 25—"Duplicate" catalysts each containing 240 mg. of palladium on 2.0 grams of charcoal; runs 26, 27—480 mg. of palladium on 4.0 grams of charcoal—catalyst divided into equal halves.

SUMMARY

A few selected substrates were reduced under arbitrarily determined but constant conditions using "duplicate" palladium-on-charcoal catalysts so that standards of catalytic activity could be established for modified catalysts.

The activities of these "duplicate" catalysts were compared by means of rate curves; in several instances wide variations were observed which were postulated to be due to random formation of "active centers".

Catalysts were prepared in double quantities and before use divided into equal halves. These "divided" catalysts in general gave results which were less reproducible than would be expected under the controlled experimental conditions employed. The cause for these differences in activity cannot be identified at this time.

When "divided" catalysts were compared to "duplicate" catalysts the variations were even greater; the random formation of active centers may be an important factor in these situations.

CHAPEL HILL, N. C.

REFERENCES

(1) LANGMUIR, *Trans. Faraday Soc.*, **17**, 617 (1922).
(2) TAYLOR, *Proc. Roy. Soc.* (*London*), **108A**, 105 (1925).
(3) ADKINS, *Reactions of Hydrogen*, University of Wisconsin Press, Madison, 1937, p. 4.
(4) REEVE AND HARTUNG, unpublished work, 1935.
(5) SHRINER AND FUSON, *Identification of Organic Compounds*, 3rd Ed., John Wiley and Sons, Inc., New York, 1948, p. 202.
(6) *Org. Syntheses*, Coll. Vol. I, 2nd ed., 63 ff. (1941).