[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, UNIVERSITY OF NORTH CAROLINA]

PALLADIUM CATALYSTS. VII.[1] INFLUENCE OF METAL-TO-CARRIER RATIO AND OF THE PRESENCE OF OTHER NOBLE METALS

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Received May 26, 1953

In the preceding paper it was postulated that during the preparation of palladium-on-charcoal catalysts there is a random and not necessarily uniform deposition of metal on the carrier, and that in the "minimal" catalysts[3] the character of these deposits has a bearing on the course of the hydrogenation reaction. Up to the present no way has been found for assuring that a second catalyst will duplicate the first in every respect even though every known precaution, such as respecting concentrations, temperatures, time, identity of materials, etc., is taken. However, there are other factors which may be controlled within the limits of reproducibility previously described,[1] and evidence for two modifications is now presented.

One of these is the ratio of metal to carrier. An indication that this is important is indicated in the previous paper,[1] where it is pointed out that for the various substrates the "minimal" catalysts have different palladium to charcoal ratios. For example, for the reduction of piperonal oxime a catalyst prepared from 240 mg. of palladium and two g. of charcoal was found optimum. For quinone the ratio could be reduced to 15 mg. of palladium to two g. of carrier. This does not mean, however, that for the conversion of quinone to quinol 15 mg. of palladium is needed, for the efficiency of the catalyst is markedly influenced by the amount of carrier employed. This is true not only for quinone but for other substrates as well. Typical experimental data are shown graphically (Figs. 1–3). It will be observed, for example, that 7.5 mg. of palladium may afford a catalyst more efficient than the earlier catalyst prepared with 15 mg. of palladium.[1]

Several likely explanations for these phenomena appear, (a) the value of n in the $(Pd)n$ clusters may vary with the amount of carrier, (b) the spacing between the $(Pd)n$ deposits may vary directly with the amount of carrier, or (c) the crystalline lattice structures of the palladium atoms may be changed when the quantity of carrier is varied. It is quite likely that all three have a bearing.

A second modification of the catalytic reaction which may be controlled within the indicated limits is found in the effect resulting from addition of other members of the noble metal group to palladium. Hartung and Chang (1) report that the addition of platinum or of rhodium to palladium influenced qualitatively the hydrogenation reaction of α-oximinopropiophenone. More recently Martin and Hartung (2) found that the amides of benzyloximino acids, *i.e.*,

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[1] For No. VI see Young, Hartung, and Daniels, *J. Org. Chem.*, **18**, 229 (1953).

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[3] A "minimal" catalyst contains sufficient palladium to produce hydrogenation over some convenient period of time, say 30 minutes to several hours.

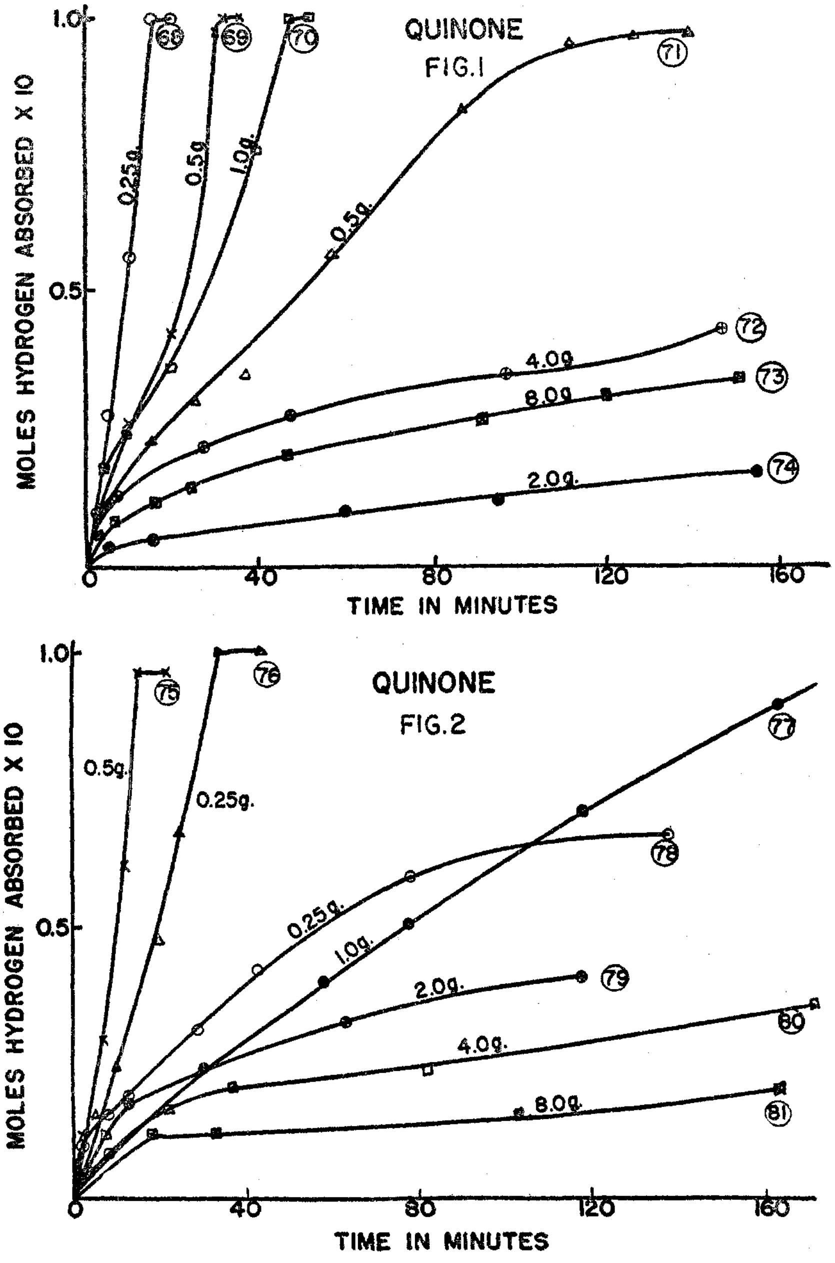

Fig. 1 and Fig. 2. Catalyst: 7.5 mg. of Palladium on Varying Amounts of Nuchar

R—C(:$NOCH_2C_6H_5$)CO—NHR′, are quite resistant when palladium alone is employed, but that excellent yields of the desired amides of amino acids,

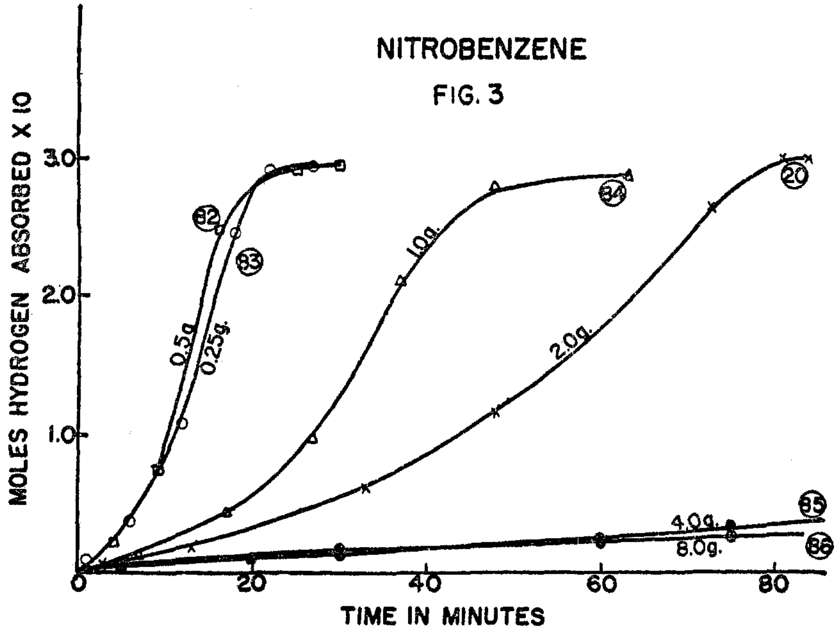

Fig. 3. Catalyst: 15 mg. of Palladium on Varying Amounts of Nuchar

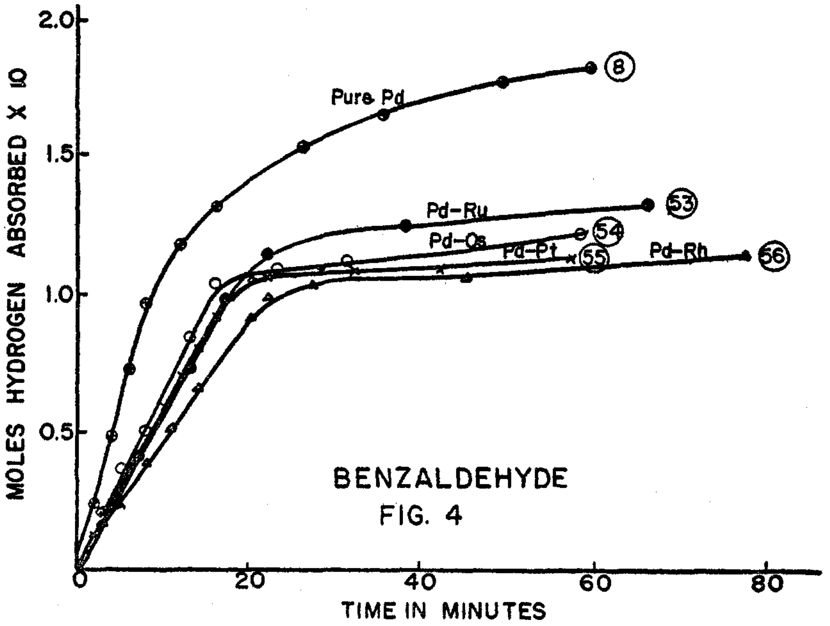

Fig. 4. Catalyst: 30 mg. of Palladium on Two Grams of Nuchar With Other Noble Ietals Added.

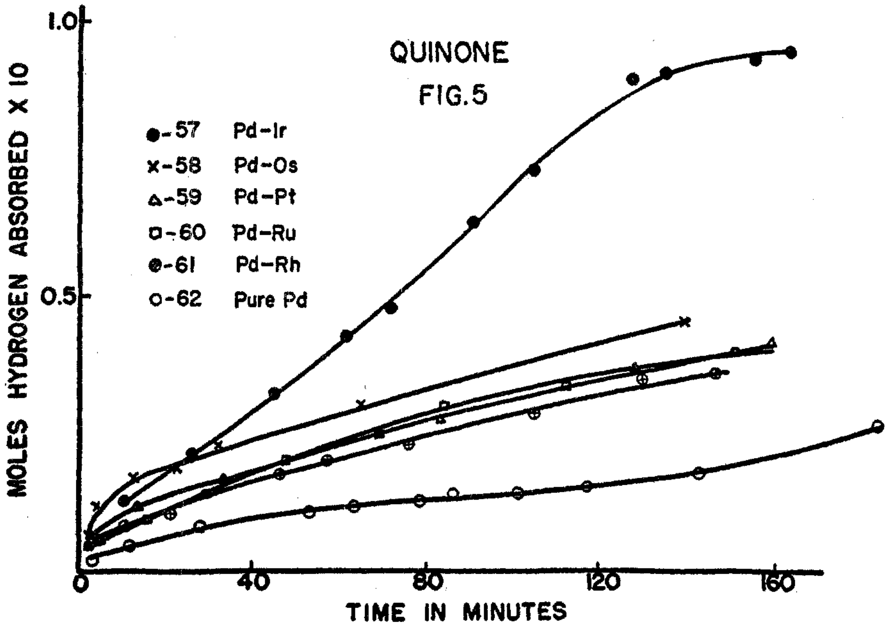

FIG. 5. CATALYST: 7.5 MG. OF PALLADIUM ON TWO GRAMS OF NUCHAR WITH OTHER NOBLE METALS ADDED.

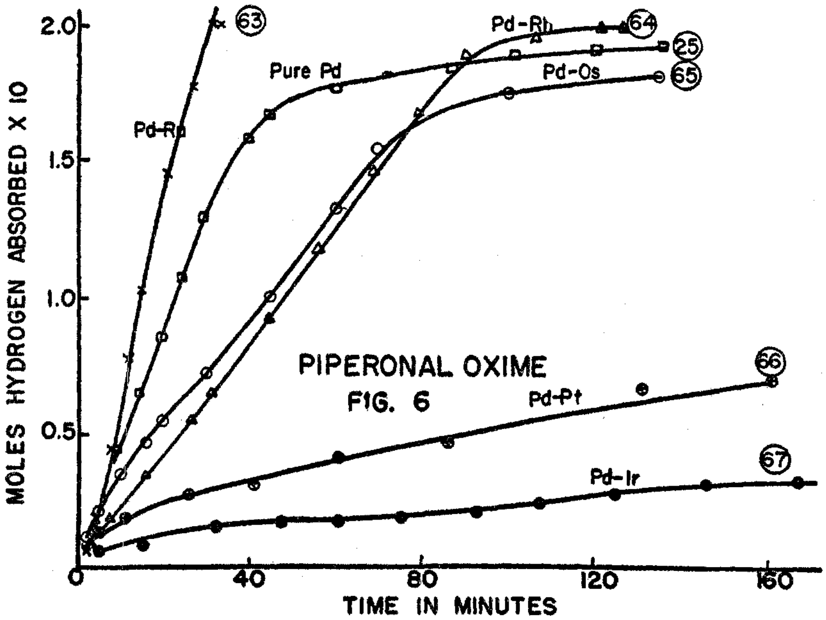

FIG. 6. CATALYST: 240 MG. OF PALLADIUM ON TWO GRAMS OF NUCHAR WITH OTHER NOBLE METALS ADDED.

(R—CH(NH_2)CONHR′, are obtained if rhodium is added to the palladium. For these reasons it was felt that studies should be made not only with rhodium but the other platinum metals as well with typical simple substrates.[4]

Representative experimental results are summarized graphically. It is to be understood that these data are also subject to the limits of reproducibility; however, check experiments suggest that the curves appear to be quite characteristic. It is interesting, not to say disturbing that present evidence indicates that a single metal may, with palladium, act as a promotor for one substrate and an inhibitor for another. For example, in the reduction of quinone (Fig. 5) all the added metals promoted the reaction, but in the case of benzaldehyde (Fig. 4), the added metals were inhibitory in every case. With piperonal oxime (Fig. 6), the reduction was promoted by ruthenium while platinum and iridium produced marked inhibitory effects.

Since in these catalysts the ratio of metal to carrier was constant, the random deposits *per se* of metal should not be unduly effected; hence, it would seem that the character of the sum total of the active centers is significantly modified, the change of character being manifested in the hydrogenation process.

EXPERIMENTAL

The procedure for preparing the catalysts has been described previously.[1]

The hydrogenation reactions were conducted in a Parr Apparatus with the initial pressure of hydrogen at four atmospheres, using one-tenth mole of substrate.

It should be emphasized that all substrates were carefully purified by distillation or recrystallization as reported previously.[1]

The platinum metals were added in a ratio of one gram-atom to 50 gram-atoms of palladium.

SUMMARY

The effect of metal-to-carrier ratio and the presence of other noble metals on the activity of palladium-on-charcoal catalysts is presented.

Changing the metal-to-carrier ratio affects markedly the course of a hydrogenation reaction carried out under carefully controlled conditions. Three explanations are suggested, (a) the value of *n* in the (Pd)n clusters varies with the amount of carrier, (b) the spacing between the (Pd)n deposits may vary directly with the amount of carrier, or (c) the crystalline lattice structures of the palladium atoms may be changed when the quantity of carrier is varied.

The addition of other noble metals to palladium-on-charcoal may affect the character of the hydrogenation reaction, whether as a promotor or inhibitor depends on the substrate.

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REFERENCES

(1) Hartung and Chang, *J. Am. Chem. Soc.*, **74**, 5927 (1952).
(2) Martin and Hartung, In press.

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[4] We are grateful to the American Platinum Works, Newark, N. J., for furnishing us with the following salts: palladium chloride (60% Pd), platinum chloride (38.31% Pt), iridium chloride (37.62% Ir), potassium osmate (51.6% Os), ruthenium chloride (34.92% Ru), and rhodium chloride (39.9% Rh).