[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

The Preparation and Properties of a Platinized Charcoal Catalyst with Some Observations on the Behavior of Inhibitors[1]

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A facile laboratory preparation of a platinized charcoal catalyst has been developed. The catalyst is notable for its inactivity in debenzylation and in dehalogenations. It appears to reduce aliphatic carbonyl compounds less readily than aromatic. Both this catalyst and palladized charcoal are inhibited toward the reduction of control substrates by bases and nucleophilic ions.

Of the various reduction catalysts employing noble metals in supported form palladized charcoals are the most frequently employed. Aside from the useful properties of these catalysts as such, their popularity is due largely to the facility of their preparation, their reproducibility and their convenience in storage and in the recovery of the metal. On the other hand, platinized charcoals appear to have been used infrequently.[2] Their properties have not been studied systematically and many of the reports concerning them have dealt with gas-phase reductions. The methods used for preparing these catalysts have not always been described but it would appear that chemical reductions or reductions with hydrogen at elevated temperatures have been employed since chloroplatinic acid is not reduced by hydrogen at ordinary temperatures.

Some years ago in a publication from this Laboratory[3] it was mentioned that a platinized charcoal catalyst can be prepared by hydrogenating in the presence of charcoal a solution of chloroplatinic acid containing a trace of palladous chloride. In the intervening time a considerable number of reductions have been carried out with this catalyst and, while much further work can still be done with profit, it is now possible to discuss its properties in a general fashion. Some of the experiments performed may have some bearing on hitherto unexplained peculiarities of other hydrogenation catalysts.

In Table I are shown the results of attempted hydrogenations of typical substrates. Since in the earliest experiments with platinized charcoal it was found that cyclohexene was reduced very rapidly, this substance was used as a standard for control purposes. After each experiment in which no hydrogen was absorbed, 5 cc. (approximately 50 mmoles) of cyclohexene was added to the reducing bottle and hydrogenation was attempted with an initial pressure of 3.7 atm. of hydrogen. Failure to observe the expected absorption (20 ± 2 mmoles/minute) was interpreted as due to poisoning or inhibition.[4] Some of the inhibitions marked in Table I notably in Reductions VIII–IX, are probably due to the basic nature of the original substrates (*vide infra*).

The general picture furnished by these experiments is of a catalyst, probably less efficient in aromatic reductions than Adams catalyst, quite inactive in dehalogenations (only allyl and benzyl chlorides were dehalogenated appreciably), normally reactive toward nitrogen–functions other than nitriles, but nearly devoid of ability to debenzylate. Hydrogenation of benzyl alcohol (IV) proceeded at a barely significant rate; dibenzyl ether, carbobenzoxyglycine and benzylmethylaniline hydrochloride were unaffected. These four compounds are among those most rapidly cleaved by palladized charcoal. It is reasonable to assume that any compound having a less labile benzyl group would survive hydrogenation with platinized charcoal, thereby permitting reduction of a more vulnerable function. Such considerations can be applied usefully, however, only in the lower temperature range and when alternative and desired hydrogenations are fairly easy. A recent attempt to hydrogenate the aromatic rings of a benzhydryl tertiary amine without breaking the N–C bond failed despite the fact that benzhydryl is considerably less subject to hydrogenolysis than benzyl.[6]

Reduction of the carbonyl function by platinized charcoal is not particularly favored. Aliphatic carbonyl compounds were reduced very slowly or not at all (XXIV, XXVI, XXVII, XXXIII, XXXV and XXXVI). Higher aromatic ketones with two rings were not reduced and in some cases (XXXVII–XXXIX) acted as inhibitors. Simpler aromatic carbonyl derivatives were reduced at slow to moderate rates, absorbing one mole of hydrogen (XXIX, XXXI, XXXIV). It is a little hard to evaluate this material since so much of the work with other catalysts has been of an occasional preparative nature. Further, as aliphatic carbonyl compounds are generally more reactive than aromatic (typically, of course, in reactions involving nucleophilic attack) it has often been assumed that a reaction observed with aromatic ketones could be generalized for aliphatic also. Palladium catalysts have often been employed to hydrogenate

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[1] Presented in part before the International Congress of Pure and Applied Chemistry, New York, September, 1951.

[2] (a) O. Hromalka, *Ber.*, **75**, 522 (1942); (b) H. J. Barber, D. H. O. John and W. R. Wragg, THIS JOURNAL, **70**, 2282 (1948); (c) C. Hansch and W. A. Blondon, *ibid.*, **70**, 1561 (1948); (d) U. S. Patent 2,411,726; (e) British Patent 594,463; (f) Y. I. Denisenko, *J. Ber. Chem. (U.S.S.R.)*, **16**, 1087 (1946); *C. A.*, **41**, 2700 (1947); (g) I. A. Musaev and G. D. Gal'pern, *Bull. Acad. Sci. U.R.S.S., Class. Sci. Techn.*, 805 (1947); *C. A.*, **42**, 1484 (1948); (h) B. A. Kazanaskii and co-workers, *Bull. Acad. Sci., U.R.S.S., Class. Sci. Chem.*, **29**, 183, 265, 473, 483 (1947); *C. A.*, **42**, 4534 (1948).

[3] R. Baltzly and A. P. Phillips, THIS JOURNAL, **68**, 261 (1946).

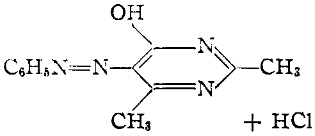
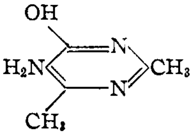
[4] In view of the studies of Maxted and co-workers[5] on the distribution of poisons between catalyst and solution, it appears theoretically possible to remove any poison from a catalyst by washing. As a practical measure, however, this is not attractive. Some substances will diminish markedly the rate of a catalytic reduction when present in appreciable concentration, but are removed by two or three washings. These are conveniently termed inhibitors. On such a basis a poison is a substance that interferes with the action of a catalyst and is not removed by a convenient amount of washing.

[5] *Cf.* especially, E. B. Maxted and H. C. Evans, *J. Chem. Soc.*, 2071 (1938).

[6] R. Baltzly and P. B. Russell, to be published.

TABLE I

TYPICAL HYDROGENATIONS WITH PLATINIZED CHARCOAL CATALYST

Reduction No.	Substrate[a]	Hydrogen absorption[b]	Products[c]
I	Cyclohexene	Very fast (1 mol)	(Cyclohexane)
II	Allyl chloride	Moderate (1 mol +)	(Propane, propyl chloride)[d]
III	Benzyl chloride	Slow (1 mol)	(Toluene)
IV	Benzyl alcohol	Very slow (*ca.* $^1/_5$ mol)	(Toluene ?)[e]
V	Dibenzyl ether	None	
VI	Carbobenzoxyglycine	None	
VII	Benzylmethylaniline hydrochloride	None	
VIII	*p*-Chloroaniline	None	
IX	*o*-Chloroaniline	None	
X	*m*-Bromotoluene	None } inhibition	
XI	*o*-Bromoanisole	Very slow	
XII	Ethyl *o*-bromobenzoate	None	
XIII	*p*-Chloro-*p*′-nitrodiphenyl ether	Very fast (3 mols)	*p*-Chloro-*p*′-aminodiphenyl ether[f]
XIV	Azobenzene + 2 mols of acetic acid	One mol very fast One mol at moderate rate	(Aniline)
XV	Azobenzene	One mol very fast One mol slowly	(Aniline and hydrazobenzene)
XVI	Azobenzene in 0.019 *N* sodium methylate	One mol very fast	Hydrazobenzene
XVII	 + HCl	Fast (2 mols)	 + (aniline)[f,g]
XVIII	Benzalmethylamine	Fast	Benzylmethylamine[f]
XIX	Anisylidene α-phenethylamine + acetic acid (1.5 mols)	Fast	*p*-Methoxybenzyl α-Phenethylamine[f,h]
XX	2,5-Dimethoxy-α-isonitroso[i] propiophenone + 3 mols HCl	Moderate (2 mols)	2,5-Dimethoxy-α-aminopropiophenone hydrochloride[i]
XXI	Benzonitrile + HCl	None	
XXII	Benzyl cyanide + HCl	None } inhibition	
XXIII	Desoxybenzoin oxime	None	
XXIV	Acetaldehyde	Very slow	(Ethanol)
XXV	Acetaldehyde + morpholine	Moderate (1 mol)	(Ethyl morpholine)
XXVI	Cyclohexanone	None	
XXVII	Acetone	None	
XXVIII	Acetone + cyclohexylamine	Very slow	
XXIX	Anisaldehyde	Moderate (1 mol)	(Anisyl alcohol)
XXX	Anisaldehyde + *n*-butylamine[n]	Slow (1 mol)	*p*-Methoxybenzylbutyl amine[j]
XXXI	*p*-Hydroxyacetophenone	Slow (1 mol)	Polymerized product[k]
XXXII	Cinnamaldehyde	Moderate (2 mols)	(Hydrocinnamic alcohol)
XXXIII	Ethyl acetoacetate[n]	None	
XXXIV	Ethyl benzoylacetate	Slow (1 mol)	Ethyl β-phenyllactate[l]
XXXV	Ethyl α-vanillylideneacetoacetate	Moderate (1 mol)	Ethyl (4-hydroxy-3-methoxybenzyl)-acetoacetate[f,m]
XXXVI	Ethyl α-veratrylideneacetoacetate	Moderate (1 mol)	Ethyl α-(3,4-dimethoxybenzyl)-acetoacetate[f,m]
XXXVII	Benzophenone	None	
XXXVIII	Desoxybenzoin	None } inhibition	
XXXIX	Benzanisoin	None	
XL	Benzene (in gl. acetic acid)	Slow (not carried to completion)	(Cyclohexane ?)
XLI	Naphthalene (in gl. acetic acid)	None (at 25°)	

[a] The solvent was methanol except as otherwise indicated. [b] Hydrogen absorption rates of 5–10 mmoles/minute are marked as *fast;* rates of 1–5 mmoles/minute as *moderate;* less than 1 mmole/minute as *slow.* [c] Products shown in parentheses were not specifically isolated but present with reasonable certainty. [d] Hydrogen chloride was also present. The hydrogen absorption could not be used directly because of the probable vapor pressure of propane. Titration of hydrogen chloride would be of little value because of methanolysis. [e] It is not impossible that this apparent debenzylation was due to contamination of the benzyl alcohol with benzyl chloride. [f] Preparative reduction. The products of XIII and XVII were isolated by Dr. Peter B. Russell, that of XVIII by Mr. Walter S. Ide, those of XXXVI and XXXVII by Miss Elvira A. Falco. [g] H. Andersag and K. Westphal, *Ber.*, **70**, 2035 (1937). [h] Isolated as the hydrochlorides prisms, m.p., 149–150°. *Anal.* Calcd. for: $C_{16}H_{20}ClNO$: C, 69.2; H, 7.3. Found: C, 69.4; H, 7.5. [i] R. Baltzly and J. S. Buck, THIS JOURNAL, **62**, 164 (1940); **64**, 3040 (1942). [j] B.p. 150° (20 mm.); b.p. 120° (1 mm.). The yield of distilled base was 75%. The hydrochloride melts at 195–196°. *Anal.* Calcd. for $C_{12}H_{20}ClNO$: C, 62.8; H, 8.8. Found: C, 63.1; H, 8.9. [k] *p*-Hydroxybenzyl alcohol is reported to polymerize on warming. This material apparently polymerized at room temperature. [l] Identified as the amide. [m] E. A. Falco, S. DuBreuil and G. H. Hitchings, THIS JOURNAL, **73**, 3758 (1951). [n] Run in parallel with palladized charcoal and with identical outcome.

ethylenic bonds selectively in compounds also containing the carbonyl function. A large proportion of such operations have been in sterol chemistry and further investigation may well reveal that aromatic carbonyls are generally more readily reduced than aliphatic by catalytic methods.[7] With platinized charcoal, at any rate, the differences are very marked. In reductions XXXV and XXXVI substituted benzylidene acetoacetic esters were reduced cleanly to the corresponding benzyl acetoacetic esters. In both cases absorption of hydrogen stopped completely after one mol had been taken up.

One of the most striking observations made in this study is illustrated by comparison of the reduction of carbonyl compounds in the presence and in the absence of primary and secondary organic bases (reductions XXIV, XXV, XXVII–XXX). In the absence of the added bases acetone was not reduced while acetaldehyde and anisaldehyde were reduced at slow to moderate rates. Further, as will be seen, bases usually inhibit the action of this catalyst (as of palladized charcoal) and, in fact, cyclohexene added to the reduction mixtures XXV, XXVIII and XXX was not hydrogenated. Nevertheless, reductions XXV and XXX proceeded satisfactorily and absorption of hydrogen in XXVIII was significant though slow. In solutions containing aldehydes and such amines, alkylolamines or Schiff bases would be present and it is evident that these substances are far more readily hydrogenated than the parent compounds. Further, it is clear that inhibition of reduction by a catalyst does not extend to inhibition of the reduction of the inhibitor itself. This is in accord with the observations of Maxted and his collaborators[5] and is not peculiar to this catalyst. Palladized charcoal also reduces mixtures of aldehydes and amines and debenzylates benzylmethylaniline and dibenzylethylamine as bases although inhibited by both substrates and reduction products toward the hydrogenolysis of benzyl alcohol.

As a result of the above it was decided to reinvestigate the matter of inhibition by bases. It had been observed previously that palladized charcoal was reversibly inhibited by bases (sodium hydroxide, pyridine and aniline), the inhibition being removed when excess acid was added. Iodide ion in considerable quantities (0.2–0.4 *N*) appeared to act as a poison.[3,4] Maxted and Evans[5] have shown that such bases as pyridine behaved as feeble poisons toward their catalysts and again the poisoning was relieved by neutralization. They suggest that simple poisons (*i.e.*, not of colloidal magnitudes) act by adsorption on the catalyst surface through attraction by their unshared electron pairs. In this theory, the removal of the inhibition of a nitrogenous base through the protonation of its last pair of electrons is analogous to the detoxification of an organic sulfide through conversion to a sulfone.

Operating on the basis of this theory, both platinized and palladized charcoal catalysts were tested with control substrates (cyclohexene for platinized charcoal, cyclohexene or benzyl alcohol for palladized charcoal) in the presence of various concentrations of methoxide, phenoxide, iodide and cyanide ions and of ammonia, benzyldimethylamine and *p*-toluidine and the half-inhibitory concentrations were determined. The results are shown in Table II. These figures are not to be taken as of high accuracy but are probably correct to within about 20% relative. The half-inhibitory concentration of cyanide is probably rather low but attempts to estimate it more closely are futile since the rate of hydrogen absorption is not constant but tends to rise. In a typical experiment wherein cyanide was 0.001 *M*, the hydrogen absorption in successive minutes was: 3.3, 5, 7.5, 10 and 12 mmoles, respectively. The most obvious explanation of this behavior is that the adsorbed cyanide ion is rapidly reduced to methylamine which is a weaker inhibitor as is also, probably, methoxide ion which should also be formed. The behavior of phenolate ion as an inhibitor is here interpreted as due to preferential adsorption on the catalyst. Such adsorption is consistent with the well-known fact that in hydrogenations of naphthols reduction of the phenolic ring is favored by alkaline conditions.

TABLE II

HALF-INHIBITORY CONCENTRATIONS OF TYPICAL BASES AND NUCLEOPHILIC IONS

Inhibitor	Molarities for half-inhibition of Platinized charcoal	Palladized charcoal
Methoxide ion	0.001	0.001
Phenoxide ion	.006	.006
Iodide ion	.0004	.0004
Cyanide ion	<.001	....
Ammonia	.002	.002
Benzyldimethylamine	.001	.001
p-Toluidine	.007	0.005–0.006

It will be seen that among the bases there is a rough parallelism between basicity and inhibiting power whereas the nucleophilic ions, or at least iodide ion, are considerably more powerful. Iodide, however, does not poison all catalysts.

It should also be pointed out that these half-inhibitory concentrations are not typical of all substrates although they may well be general for those having no points of attachment of high electron density. Nitrobenzene was reduced rapidly to aniline in methanol 0.019 *M* in sodium hydroxide (or methoxide). Alkali also permitted ready reduction of azobenzene—but only one mol of hydrogen was absorbed, hydrazobenzene being the product of reduction. This is in general agreement with past experience since it is known that the reduction of azobenzene proceeds more rapidly than that of hydrazobenzene: Skita[8] and Brand and Steiner[9] have reported the preparation of hydrazobenzene by partial reduction of azobenzene. In both papers it is stated that a second mol of hydrogen is absorbed much less rapidly than the first. Skita operated with colloidal palladium in *alkaline solution*. Brand and Steiner reduced with palladized charcoal in neutral solution and interrupted the reduction after one mol of hydrogen had been absorbed. In neutral

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[7] W. P. Dunworth and F. F. Nord, THIS JOURNAL, **74**, 1459 (1952).

[8] A. Skita, *Ber.*, **45**, 3312 (1912).

[9] K. Brand and J. Steiner, *ibid.*, **55**, 875 (1922).

solution, platinized charcoal reduced azobenzene to hydrazobenzene very rapidly, the second mol of hydrogen being taken up rather slowly. In the presence of acid the first stage of reduction is not much affected but the second is greatly aided (XIV–XVI). It would appear that the inhibitor competes successfully for the catalyst surface with hydrazobenzene, but not with azobenzene. It is also possible that in reduction XV aniline formed by hydrogenolysis may inhibit further reduction of hydrazobenzene.

While it should sometimes be possible to employ inhibitors for selective reductions, this is not always the case. It would appear that in the reduction of azobenzene to aniline two separate adsorptions and reductions are involved. In other cases a function to be reduced may pass through all stages of reduction in one adsorption. Thus in the hydrogenation of phenylacetylene by platinized charcoal there is no change in the reduction rate at the half-way point. In the presence of 0.01 M *p*-toluidine this situation was unchanged and in 0.01 M sodium methoxide the reduction was actually more rapid throughout (perhaps due to favored adsorption of phenylacetylide anion). Similarly with methyl acetylenedicarboxylate: there was no break in the reduction either in neutral solution or with *p*-toluidine present in 0.03 M concentration and the rate of hydrogen absorption was effectively the same in both experiments.

Experimental

Preparation of Platinized Charcoal.—All batches of catalyst were prepared in identical fashion. One g. of charcoal (Darco G-60) was placed in a reducing bottle (for the usual Burgess–Parr hydrogenator). Water (30–50 cc.) was added and solutions of chloroplatinic acid and palladous chloride containing, respectively, 100 mg. of platinum and 0.2 mg. of palladium. The bottle was placed on the hydrogenator, evacuated, filled with hydrogen (pressure not critical) and shaken for 15–20 minutes. On removal, the water was taken off and replaced with methanol.

The catalyst is stored and treated in the same fashion as palladized charcoal. It probably can be dried and kept in a vacuum desiccator but that technique has not been used in this Laboratory. It can be filtered and washed on a buchner with the usual precautions but it is rather more convenient to remove solvent by suction through a filter tube. This process requires more elapsed time but less working time and obviates any danger of ignition.[10] When not in use the catalyst is stored under methanol in a reducing bottle. Each batch of catalyst was used as a unit throughout without subdivision. As with palladized charcoal, the life of a batch of catalyst is indefinite and depends largely on some fortuitous incident of poisoning. When apparently poisoned a batch would usually be washed with acid in hope of re-activating it. While such procedures were sometimes successful it is easier to recover the metal and start fresh than to attempt detoxification as a serious measure.

Reductions.—Hydrogenations were performed in methanol and at room temperature except as otherwise stated in Table I. Usually 50 mmoles of substrate was dissolved in 50 cc. of methanol. In run XXV, 50 mmoles of morpholine was used together with a considerable excess of acetaldehyde.

Reduction products were isolated when they were expected to be new compounds or if their identity was in doubt. The immediate product of reduction XXXI was probably *p*-hydroxy-α-phenethyl alcohol. In working up the product, however, only polymeric materials could be obtained.

Inhibition Studies.—The determination of the half-inhibitory concentration of a substance involves certain complications, probably due to the ability of the catalyst to absorb or otherwise entrain appreciable quantities of acid or alkali. Thus early approaches to the problem by adding to the solution before reduction a quantity of standard alkali sufficient to produce the desired concentration led to erroneous results when the approach was made from the low *p*H side. This was not realized until the attempt to revive a completely inhibited catalyst required far more washing than had been anticipated.

A technique that eventually proved satisfactory was to employ a concentration of inhibitor that largely suppressed the reduction of cyclohexene and by diluting this solution with portions of methanol and sucking off the supernatant solvent to the 50-cc. level, gradually to determine an approximate half-inhibitory level. At this point the catalyst was mixed with rather large volumes (*ca.* 200 cc.) of specific concentrations of alkali (sodium hydroxide in methanol) and in each case allowed to stand with occasional shaking for a relatively long period (15–50 hours). Solvent was then removed to leave 50 cc., cyclohexene was added and the rate of hydrogenation observed. Similar procedures were followed with the other inhibitors. For example, with ammonia, a 0.1 M solution produced complete inhibition. After successive dilutions, about 25% of normal activity was observed when the ammonia concentration was 0.005–0.01 M. Equilibration with 0.005 M ammonia gave about 30–40% of normal activity, whereas 0.002 M ammonia consistently gave 50% of the usual rate of reduction.

It was expected that when ammonium chloride was added to such a half-inhibitory concentration of ammonia, the rate would increase. Actually it diminished. This might be due to the existence of molecular ammonium methoxide (analogous to ammonium hydroxide) which was itself an inhibitor. At any rate, it is clear that the inhibition by ammonia in methanol is not due to methoxide ion.

An additional complication which made these inhibition studies unexpectedly laborious was that solutions of inhibitors that largely inactivated the catalyst tended to produce colloidal solutions. Addition of acid reversed this process but the acid had then to be washed out before again approaching a half-inhibitory concentration. Palladized charcoal showed little or no tendency to become colloidal under the same conditions.

For the various inhibitors, ammonia, benzyldimethylamine, *p*-toluidines, potassium iodide and sodium cyanide were made up as standard solutions in methanol. Sodium methoxide was prepared by adding concentrated carbonate-free sodium hydroxide solution to methanol, the concentration being determined as 0.019 M by titration. No attempt was made to differentiate between hydroxide and methoxide but the latter must have predominated. The desired phenolate concentrations were obtained by adding appropriate quantities of standard methoxide to the reduction mixtures which were 0.05 M in phenol.

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[10] When this technique is applied to palladized charcoal the blank adsorption of hydrogen by the catalyst (0.6 g. of Pd on 6 g. of charcoal) diminishes from 5–6 to 1–2 mmoles presumably because the adsorbed hydrogen remains on the catalyst. With platinized charcoal in the quantities used the blank absorption is not over 1 mmole in any case.