104 instrument using electrical scanning, with normal and low-voltage electron energies set at 70 and 7.5 eV nominal, and with inlet and source temperatures of 350 and 250 °C, respectively. Directly coupled gas chromatography–mass spectrometry utilized a 5 ft × 0.125 in. stainless steel column packed with 10% SE-30 on Chromosorb W, coupled via a jet-orifice separator to a Du Pont Model 21-491 mass spectrometer; electron energy was 70 eV and ion source temperature was 250 °C.

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Registry No.—Silver benzoate, 532-31-0; sodium benzoate, 532-32-1; silver *p*-fluorobenzoate, 57665-04-0; sodium *p*-fluorobenzoate, 499-90-1; silver pentafluorobenzoate, 3796-31-4; sodium pentafluorobenzoate, 4830-57-3; silver 2-pyridinecarboxylate, 27876-60-4; sodium 2-pyridinecarboxylate, 57665-05-1; silver 3-pyridinecarboxylate, 57665-06-2; sodium 3-pyridinecarboxylate, 54-86-4; silver 4-pyridinecarboxylate, 57665-07-3; sodium 4-pyridinecarboxylate, 16887-79-9; Na_2 terephthalate, 10028-70-3; Na_2 isophthalate, 10027-33-5; Na_3 trimellitate, 50976-34-6; Na_3 trimesate, 17274-08-7; Na_4 pyromellitate, 148-04-9; Na_5 benzenepentacarboxylate, 145-45-9; Na_6 mellitate, 145-44-8; Na_2 napthalene-2,6-dicarboxylate, 16303-32-5; Na_2 pyridine-3,5-dicarboxylate, 57665-08-4; Na_2 thiophene-2,5-dicarboxylate, 57665-09-5; silver nitrate, 7761-88-8.

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Studies on Catalytic Hydrogenation. I. The Influence on Reaction Rates of the Metal–Carrier Ratio of Solvents and Acidity[1]

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It is shown that in aqueous methanolic and aqueous acetic acid solutions catalytic hydrogenations of a variety of substrates can be conducted at rates independent of hydrogen pressure and substrate concentration. The pressure above which hydrogen availability ceases to be limiting is about 3 atm. Substrate adsorption is a function of the activity (and an inverse function of the solubility) of the substrate in the solvent. Platinum, palladium, and rhodium adsorbed on carbon (charcoal and powdered graphite) were examined. Platinized carbon is highly sensitive to acidity, palladized carbon only in the reduction of C–O functions. Rhodium on carbon is somewhat inhibited by acidity in reductions of benzene and acetophenone and indifferent to acidity in the reduction of cyclohexene. The efficiency of various metal–carrier ratios varies somewhat with the substrate, especially with rhodium. Metallized graphites resemble closely the corresponding metallized charcoals but require 10–20 times as much carrier.

This investigation had a dual purpose: to provide a basis of standard catalyst activity for poisoning studies and to relate the behaviors of metallized charcoals and graphites.[2] For both projects it was necessary to have more knowledge of the reaction kinetics and the effect thereon of the solvent medium.

The kinetics of catalytic hydrogenation of nitro compounds in aqueous alcoholic solutions have been studied by Yao and Emmett[3] and of cycloalkenes in cyclohexane by Hussey and his co-workers.[4] Both groups gave extended discussions of theoretical and experimental kinetics. For the present purpose eq 1

$$\text{rate} = \frac{\text{mmol}}{\text{min}}\,H_2 = Akw\theta_H\theta_S \qquad (1)$$

is proposed as valid when small amounts of catalyst are used. Here A is a constant containing factors dependent on the solubility of hydrogen in the solvent, the viscosity and surface tension of the solvent, and the efficiency of mixing.[5] w and k are the weight of catalyst (in default of the unknown surface area) and the real constant of hydrogenation and θ_H and θ_S are adsorption terms for hydrogen and substrate.[6]

In extended form, the substrate adsorption term

$$\theta_S = \frac{\alpha_s C_s}{\beta + \alpha_s C_s + \alpha_{SH} C_{SH} + \Sigma \alpha_{sv} C_{sv} + \alpha_i C_i}$$

where β is a constant,[7] the C symbols refer to concentrations of substrate, reduced substrate, solvents, and inhibitor, if any, and the α symbols are the appropriate adsorption coefficients. The term $\alpha_{SH}C_{SH}$, if sizable, corresponds to product inhibition, frequently observed with enzymes. It is probably not significant in the present work except in the reduction of nitrobenzene. Consideration of $\alpha_i C_i$ is to be taken up later. In the absence of poison or product inhibition

$$\theta_S = \frac{\alpha_s C_s}{\beta + \alpha_s C_s + \Sigma \alpha_{sv} C_{sv}}$$

and two simple methods of treatment are available.

Yao and Emmett chose to regard the denominator as

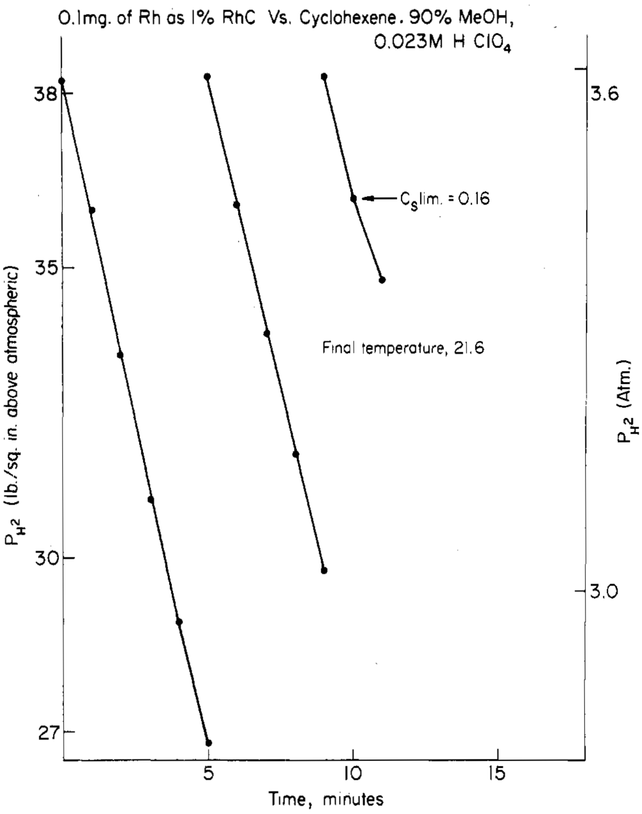

Figure 1.

large in proportion to $\alpha_s C_s$ leading to a rate first order in substrate concentration. They achieved this in part by operating in rather dilute solutions but reported that increase in the water content of the solvent favored lower order kinetics. The alternative is to regard $\alpha_s C_s$ as large in relation to β and the solvent-adsorption term, in which case θ_s approaches 1 and may be experimentally indistinguishable from 1 over a convenient portion of the reduction. This treatment leads to the function C_s lim, defined as that concentration of substrate above which zero-order kinetics are observed. For this, the solvent adsorption terms need not be zero. In the work of Hussey and coworkers, using cyclohexane as solvent, $\Sigma \alpha_{sv} C_{sv}$ could well have been zero. They reported that platinum on alumina reduced cycloalkenes with zero-order kinetics almost throughout. This was not the case with palladized alumina: Figure 1 of ref 4b suggests C_s lim around 0.35 (not far from the figure given in Table IIb of the present communication). In the present work, cyclohexene appeared more strongly adsorbed by platinized charcoal than by palladized charcoal (and more strongly on Rh/C than on the other catalysts). The differences, however, are not sufficient to account for the large variations reported by Hussey, with, of course, markedly different catalysts. In the present studies operations were feasible above C_s lim with the possible exceptions of the reduction of benzyl alcohol by Pd/C and of benzene and acetophenone by Rh/C.

The hydrogen adsorption term

$$\theta_H = \frac{\alpha_H P_{H_2}}{\beta + \alpha_H P_{H_2}}$$

The denominator may contain further adsorption terms corresponding to those of θ_s. Similar simplifying assumptions can be applied leading to kinetics of first order in hydrogen or to kinetics of lower order. Most accurate work has been done with constant-pressure apparatus which does not accommodate large pressure variations. As a consequence, most experiments were at atmospheric pressure with a very few explorations of the effect of lower hydrogen pressures and of higher pressures up to 1.5 atm.[4a] Within this range, Yao and Emmett found their rates proportional to hydrogen pressure, as did Hussey et al. with platinized alumina. However, Hussey and Nowack reported lower orders of hydrogen dependence with palladized alumina.

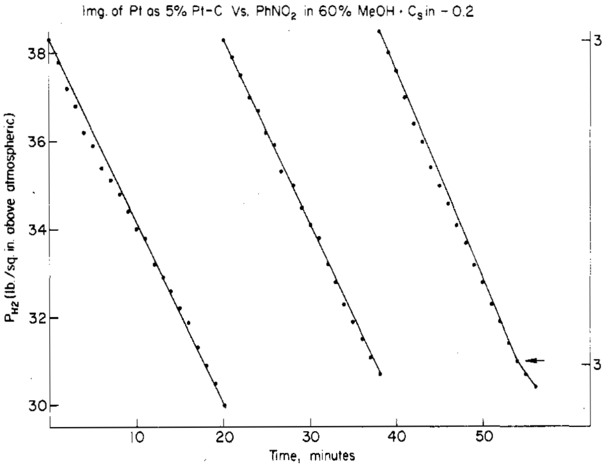

Figure 2.

Since, in principle, hydrogen pressure is capable of very large variations, one may postulate some hydrogen pressure, P_{H_2} lim, above which θ_H should be experimentally equal to 1. Whether this pressure would be accessible with the available apparatus was not a priori predictable. In the present work, above about 3 atm of hydrogen pressure, it was found that pressure drop was linear with time so that work was possible above both P_{H_2} lim and C_s lim. This is especially advantageous when dealing with poisoning phenomena.[8]

With Pd/C and Rh/C, P_{H_2} lim appeared appreciably lower than with Pt/C. The value of this function is probably dependent on the solvent, the apparatus, and the hydrogen demand, although in the present work no correlation with this last factor was noted. No attempt was made to study its variation further after finding that a P_{H_2} lim exists and is accessible. Figures 1 and 2 give plots of two reductions illustrating the determinations of C_s lim and the constancy of the pressure drop above P_{H_2} lim.

The value of C_s lim depends heavily on that of α_s, which is, in general, unknown. However, α_s should be dependent on the thermodynamic activity of the substrate (equated to 1 as a pure substance). Since most organic substrates are sparingly soluble in water, α_s should increase with the water content of the solvent mixture and C_s lim for such substrates should diminish. Figure 3 shows the plot of the concentrations of nitrobenzene in saturated solution and C_s lim of nitrobenzene in 60–75% methanolic solutions. The general similarity of the two curves is obvious.

Choice of Substrates. It was desired to have substrates typifying a number of the functions of major interest. Stability of the substrate was also advisable; however, cyclohexene was selected for study despite the difficulties in dealing with it because of the studies of Hussey.[4] Some olefene was desired, and there was no reason to prefer another of this class. Nitrobenzene and acetophenone were also used with all the metallized charcoals.[9] The reduction of benzene was examined with rhodium on charcoal and hydrogenolysis of benzyl alcohol with palladized charcoal. The results of poisoning studies with benzyl alcohol led to the examination of benzaldehyde with the same catalyst. A limited amount of work was done with benzyl methyl and benzyl isopropyl ethers in order to correlate the benzyl alcohol results with other substrates for debenzylation.[10]

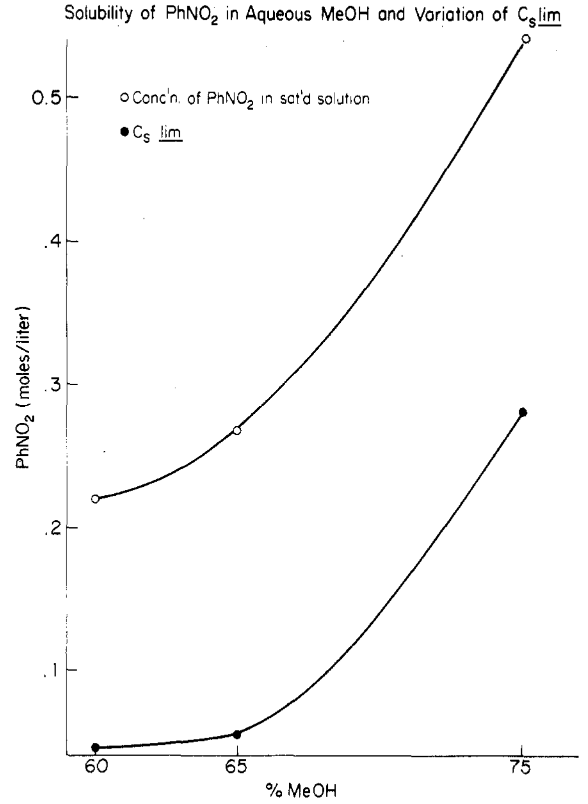

Figure 3.

Experimental Section

Apparatus. Reductions were performed in an Adams-Burgess-Parr reducer having a pressure gauge registering the pressure in the isolated shaking bottle (volume 400 ml). This gauge was marked at intervals for 1 psi and could be read with fair accuracy to 0.1 lb. A pressure drop of 1 psi corresponds very closely to 1 mmol of hydrogen when the volume of solution is 50 ml, as in all kinetic runs here reported. The rate of shaking was 170 ± 10 strokes/min.

Temperature Control. Initially this was one of the major problems since considerable amounts of heat were liberated in a moving, thick-walled glass vessel. No method of thermostating by a circulated fluid *at* the desired temperature was likely to be adequate. Fortunately, the heat produced must be proportional to the rate of hydrogen consumption. The heats of hydrogenation of benzene and cyclohexene are known accurately.[11] Those for the hydrogenation of nitrobenzene to aniline, benzyl alcohol to toluene, and C=O to CHOH can be deduced less certainly from combustion data. From these it appears that the heat liberated per H_2 *absorbed* in these reductions varies in the proportion cyclohexene, 1; nitrobenzene, 1.5; acetophenone and benzaldehyde, 0.5; benzene, 0.6; and benzyl alcohol, 0.9.

Cooling was accomplished by placing a strip of wet paper toweling around the shaking bottle under the protective wire screen. The strip could be varied in size and cooling increased (up to about a third) by projecting a variable air stream upon the shaking bottle. Before beginning a day's run, a bottle containing 50 ml of water initially at 22 °C was shaken for 5 min while cooled by a standard strip (13 cm in width), and the fall in temperature was recorded. With this as a guide, the cooling requirement for an expected rate of hydrogen absorption could be selected. The temperature of the solution was set at 22 °C immediately before hydrogenation[12] and redetermined at the end. Runs in which the deviation was more than 1 °C were discarded.[13]

At the start of a run, after evacuation, shaking was started and hydrogen admitted rapidly to the desired level (ca. 3.5 atm). The first reading was made about 10 s after full pressure had been attained. When more hydrogen was introduced, this was done without stopping the motor, and the first reading of the new series was made after a 10-s interval. Pressure readings were made 1 min apart, and a record was made of the variable air stream (for cooling) when it was used. In general, a run was terminated soon after the rate of pressure drop had departed significantly from linearity, and the temperature of the reduction mixture was redetermined.

Substrates. Benzyl alcohol and benzaldehyde were commercial grades (the latter freed of benzoic acid). It was not certain that the benzyl alcohol was completely free of poison since the available solvent conditions were limited, and it was not certain that a true C_s lim had been determined. The amount of contamination could not have been large. A commercial sample of benzyl methyl ether, on the other hand, was obviously poisoned as was the same material prepared in this laboratory and benzyl isopropyl ether,[14] when prepared from commercial benzyl chloride. These ethers could be obtained in satisfactory condition by recovery from partial reductions with larger amounts of catalyst or by synthesis using benzyl chloride prepared by chloromethylation of pure benzene.

Commercial nitrobenzene and acetophenone were quite unusable. Both were generally prepared by synthesis from pure benzene. For this purpose a small Friedel–Crafts reaction (ca. 0.5 mol of acetyl chloride) was run in about 1 l. of "thiophene-free" benzene. The acetophenone from this reaction was discarded, and the recovered benzene was suitable for nitration and acetylation reactions and as a substrate for Rh/C reductions. The nitrobenzene and acetophenone so prepared were distilled thrice in vacuo through a 25-cm Vigreux column. Both were stable without special precautions.[15,16]

Cyclohexene is a troublesome substrate: Hussey and co-workers[4] have described the extreme precautions necessary (but not always sufficient) for their very precise operations. The possible accuracy in the present work being less, it was found generally sufficient to *distill under nitrogen each day a sample sufficient for the runs to* be attempted. The distillate was kept under nitrogen until used. The first run on each sample was always a control. Batches were not always satisfactory: inferior material was often usable in orienting runs for locating half-poisoning concentrations. A few bottles *of cyclohexene were of good quality when first opened. In such* cases, the contents were protected as well as possible with nitrogen and used as long as satisfactory controls could be obtained.

The precautions for operations on cyclohexene with platinum and palladium were less frequently adequate with rhodium. In *part, this is a function of the high activity of Rh/C in this reduc*tion. Whereas 1 mg of Pt and 0.5 mg of Pd were the standard amounts for cyclohexene reductions, only 0.1 mg of Rh was used. Thus, an amount of poison capable of depressing the reduction rate of Pt or Pd by 5% would be expected to lower the Rh rate by 25%.

On the Nature of the Contaminants in Cyclohexene. On long standing a considerable amount of thickish and presumably polymeric material accumulates in bottles of cyclohexene. This can be removed by distillation, but such purification is not enough. It is clear that rapidly forming poisons of low molecular weight are present, owing their origin to traces of oxygen and (probably) light.

Some further information was obtained fortuitously. An inferior sample of cyclohexene was used in orienting experiments on poisoning by manganous ion. As small, but increasing amounts of manganous chloride were employed in successive runs the rate *increased* to, but not above, the best standard rate. Still larger amounts of manganese resulted only in poisoning. It was found that as a rule when the control run on a newly distilled sample of cyclohexene was not depressed more than a third below the standard rate, it was possible to regain the normal rate by use of manganous chloride, which seemed to operate at least roughly in a stoichiometric fashion. The concentrations of Mn^{2+} required were in the order of 10^{-4}, which is twice the half-inhibitory concentration of Mn^{2+} with pure cyclohexene.

It thus appeared likely that the manganous ion was acting as a scavenger, being itself oxidized to a higher valence not reducible under the conditions. This effect was not manifested by zinc and cadmium, which have only one ionic valence. A further indication about the toxic contaminants is that this manganese effect is not manifested when the manganese is added *after* the reduction has begun. The manganese must be present at the start and the evacuated reduction bottle shaken for 2 or 3 min before admission of hydrogen (the usual procedure in poisoning experiments).

Thus it appears that cyclohexene can contain at least two toxic contaminants not readily separated by *fractional distillation*, both presumably derived from the attack of oxygen on the substrate. The one can be decomposed by shaking with catalyst and manganous ion and is reducible to a poison not so decomposed. Since not all distilled samples could be so restored, at least one other poison is probable. Some at least of the poisons tend to be adsorbed on activated alumina.

The manganese effect was prominent with Pt/C, much less so with Pd/C, and absent with Rh/C. Manganous ion is a moderately strong poison against cyclohexene with Pt/C ($C_{\mathrm{i}\,1/2} = 5 \times 10^{-5}$),[17] very much weaker with Pd/C ($C_{\mathrm{i}\,1/2} > 6 \times 10^{-3}$), and substantially nontoxic with Rh/C. It is thus probable that the scavenging action takes place on the catalyst.

Preparation of Catalysts. Platinum and palladium were portions of rather large stocks in the author's possession. Platinum was purified by precipitation as $(NH_4)_2PtCl_6$ and recrystallization of that salt from water containing a little NH_4Cl. Palladium was purified by alternate precipitation as $Pd(NH_3)_2Cl_2$ and $(NH_4)_2PdCl_6$.

When needed, the appropriate amounts of $(NH_4)_2PtCl_6$ and $(NH_4)_2PdCl_6$ were weighed into a porcelain crucible, ignited, and converted via HBr–aqua regia and HCl treatments to chloroplatinic acid and palladous chloride. These residues were dissolved in water containing a little excess hydrochloric acid and made up to volume so that 1 ml contained 1 mg of metal.

Rhodium was in the form of a commercial sample of $RhCl_3 \cdot 3H_2O$. A solution was made up to 250 ml containing 639.8 mg of this salt and 1 ml of 1 N HCl, thus containing 1 mg of Rh/ml. A more dilute solution was prepared containing 0.2 mg of Rh/ml. In order to have a substantially chloride-free solution, 25 ml of the 1 mg/ml solution plus 0.1 ml of 70% $HClO_4$ was evaporated to a syrup in a rotary evaporator and made up to 25 ml.

Palladized charcoal was prepared by shaking an aqueous solution containing the desired amount of palladous chloride with a weighed quantity of charcoal[18] under hydrogen.[19]

Platinized charcoal was prepared by two methods. One, in which a trace (1 atom:500) of palladium is present in the chloroplatinic acid solution to initiate deposition of metal,[20] gave a preparation referred to here as Pt/C (B). Later, an alternative preparation, Pt/C(Z), was studied. This was based on the work of Zeliger.[21] The difference is that no palladium initiator was present. The two preparations were equivalent in most respects.[22]

In the course of the present work, it was found that both platinum and palladium are strongly adsorbed on charcoal in equilibrium with the solutions used. If this was also the case with the carriers used by Zeliger, it is probable that reduction of the chloroplatinate ion occurs only on the surface of the carrier and that the metal is not picked up by the carrier from a colloidal state. Some support to this hypothesis may be drawn from the deposition of metal on the inside of the glass reaction vessel. This was very rare with platinum, infrequent with palladium, and almost invariable with rhodium. Experiments on the adsorption of the metal ions by the carrier indicate that under the conditions of the preparation, about 90% of the palladium, 75% of the platinum, but only 25% of the rhodium is resident on the charcoal before hydrogen is admitted.

Rhodium on charcoal was prepared by the same method as with palladium. That prepared in this laboratory is symbolized as Rh/C. Catalyst E was a "5%" Rh/C obtained from Engelhard (lot 14 269).

The metallized graphites were prepared in the same fashion as the corresponding metallized charcoals. The powdered graphite used was "special spectrographic graphite powder" grade SP-2 (lot 302) obtained from the National Carbon Co. Some preparations employing very large amounts of carrier were made using some methanol in the solution. These preparations were apparently satisfactory, but were regarded with some suspicion since catalyst preparation is not feasible from high (ca. 75%) concentrations of methanol.

All the catalysts prepared here were shaken under hydrogen at least 30 min. This is probably an excessive time. One suspects that Pt/C(Z) may be formed more slowly than the B variety, but an attempt to determine the time involved by preparing the catalyst in 75% methanol with nitrobenzene present failed; virtually no catalytic activity resulted.

For nitrobenzene reductions an extra step was required for consistent results. After the catalyst had been prepared, the shaking vessel was evacuated, air was admitted, and shaking was resumed for 15 min (again, probably an excessive time) to remove traces of hydrogen. In the absence of this step, rates were erratic. The probable point is that when some hydrogen is on the catalyst when nitrobenzene is added, there is some reduction while oxygen is still present and oxidation of the reduction products produces poison. If strong acid is to be added in the reduction, this should be done after this aeration step.

Solvents. A few reductions of benzaldehyde were done in 2-propanol, the others in methanol or acetic acid and their mixtures with water. The water was distilled in glass. Commercial methanol, 2-propanol, and acetic acid were found satisfactory.[23] Since the catalysts were prepared in aqueous solution (5–10 ml), direct addition of solvent sufficed to give up to 90% solutions (v/v). For higher concentrations, the initial preparation was diluted to ca. 350 ml with solvent, equilibrated, and allowed to settle. The supernatant was then removed (to 10 ml) through an upturned capillary. Addition of the required amount of solvent gave the desired composition for the reduction mixture. This operation was used mainly with platinum catalysts since the stability of palladium and rhodium under the conditions was doubtful. When used with these metals, the settling out process was carried out under hydrogen.

Solubilities and Choice of Substrate Concentrations. Substrate concentrations were chosen with the aim of having a reasonable range showing a zero-order rate. The upper limit of substrate concentration was taken as 20% (10 ml in 50 ml). Solubilities of the substrates used and of some reduced substrates were determined by placing a known volume of the substrate in a graduated cylinder and adding solvent in portions until all dissolved. The charge was chosen so that there should be only one liquid phase. Thus, in reductions of nitrobenzene in 75–99% methanol, the starting substrate concentration (C_s in) was 0.39 M, 0.23 in 65% methanol, 0.2 in 60% methanol, and 0.18 in 60% methanol 1 M in NaCl.

There are certain practical limitations in solvent composition. While all the substrates used are more soluble in methanol and acetic acid than in water, and, in principle, it should be possible to lower C_s lim to any desired level by using a more aqueous solvent, the properties of the reduced substrate must also be considered. This complication does not arise with aniline or α-phenethyl alcohol, but cyclohexane is much less soluble in aqueous solvents than cyclohexene and benzene. Similarly, toluene is less soluble than benzyl alcohol and the two benzyl ethers studied. Benzyl alcohol was examined in 80 and 90% methanol and in 75% acetic acid. Second liquid layers could be avoided by not carrying the reductions too far, but it is not certain that C_s in exceeded C_s lim. The benzyl ethers gave satisfactory zero-order rates in 75% acetic acid, but C_s lim was doubtful in 80% methanol. Reductions of benzene in 80% methanol gave indications of a second phase and 85% methanol was the solvent of choice, even though C_s lim was very close to C_s in.

Purity of Substrates. Hussey and co-workers[4] imposed very rigid criteria: that three successive charges of substrate could be hydrogenated over the same catalyst and in the same solution and give the same rate within the limit of other experimental errors. This was feasible in their experiments since their substrates, on reduction, became identical or substantially identical with the solvent. When this would not be the case, this criterion cannot be applied.

A second criterion proposed originally was that one should be able to reduce a charge of substrate, dilute with solvent, draw off the supernatant after the catalyst had settled, restore the original conditions, and obtain the same rate with a fresh charge. This operation is, in fact, feasible with Pt/C and cyclohexene provided that the first charge of substrate is completely reduced. However, since the cyclohexene was redistilled each day and not all samples were acceptable, this criterion was at best inconvenient. This criterion was never regarded as applicable to nitrobenzene since traces of oxygen produce toxic substances very rapidly from aniline in the presence of catalyst. The test was tried with varying but not complete success for awhile with acetophenone. It was never possible to match the second rate with the first, and the attempt was abandoned when it was found that the discrepancy *increased* when the first charge had been completely reduced. This suggests that the deterioration is due to some reaction of α-phenethyl alcohol.

No attempt was made to apply this test with palladium and rhodium catalysts since it was doubtful whether one could expect the integrity of the catalyst surfaces to be maintained in the presence of even traces of acid.

The third test requires that the rate should be proportional to the amount of catalyst with small amounts of the latter. Thus, for nitrobenzene and cyclohexene, runs were compared with 0.5, 1, and 1.5 mg of Pt, with acetophenone runs with 5, 10, and 20 mg of metal. Having found such proportionality, standard zero-order rates under various conditions were established, and later samples of substrate were required to meet the standards of these rates.

Amounts of Catalysts. Throughout this communication the amount of catalyst is given as the amount of metal, and the percentage refers to the (wt of metal × 100)/wt of carrier. Thus, 1 mg of 5% Pt/C means 1 mg of Pt on 20 mg of charcoal; 5 mg of 3% Pd/C means of 5 mg of Pd on 165–170 mg of charcoal, etc.

It has already been shown abundantly (cf., among others, ref 3, 4) that significant rates are obtainable only with small amounts of

Table I. Standard Zero-Order Rates of Hydrogenation with 5% Pt/C ("Old" Darco)

Solvent	Acidity (or electrolyte)	Rate, mmol H_2/min	C_S lim
A. Substrate Nitrobenzene, 1 mg of Pt: C_S in = 0.39			
99% MeOH	Residual (res)	2.14	0.31
95% MeOH	Res	2.15	0.26
75% MeOH	Res	1.4	0.28
65% MeOH[a]	Res	0.67	0.05–0.06
60% MeOH[b]	Res	0.42	0.045
95% MeOH	0.72 M H_2SO_4	2.35	0.22
95% MeOH	0.72 M HCl	1.37	0.2
75% MeOH	0.72 M H_2SO_4	1.7	0.14
75% MeOH	0.46 M $HClO_4$	1.6	0.16
75% MeOH	0.6 M HCl	0.93	0.14
75% MeOH	0.38 M NaCl	1.0	0.20
65% MeOH[a]	0.36 M H_2SO_4	1.02	0.09
65% MeOH[a]	0.38 M HCl	0.67	0.075
65% MeOH[a]	0.38 M NaCl	0.54	0.05–0.06
60% MeOH[b]	0.72 M H_2SO_4	0.8	0.05
60% MeOH[b]	1.0 M HCl	0.57	0.07
60% MeOH[c]	1.0 M NaCl	0.43	0.04
99% MeOH	Neutral	1.4	0.32
75% MeOH	Neutral	0.7	0.32
65% MeOH[a]	Neutral	0.6	0.07
99% HAc	Res	0.54	0.34
75% HAc	Res	0.74	0.26
60% HAc	Res	0.64	0.21
50% HAc	Res	0.44	0.21
89% HAc	0.46 M $HClO_4$	0.73	0.37
75% HAc	0.46 M $HClO_4$	0.93	0.3
75% HAc	0.48 M HCl	0.57	0.31
B. Substrate Acetophenone, 10 mg Pt: C_S in = 1.7			
99% MeOH	Res	1.9	1.5
99% MeOH	Neutral	0.7	1.6
75% MeOH	Res	1.86	1.12
75% MeOH	0.36 M HCl	1.46	1.46
75% MeOH	0.36 M $HClO_4$	2.0	1.3
75% MeOH	Neutral	0.6	1.45
65% MeOH	Res	1.7	1.2
60% MeOH	Res	1.12	1.1
75% HAc	Res	1.0	1.5
60% HAc	Res	1.1	1.2
C. Substrate Cyclohexene, 1 mg Pt [3% Pt/C (B)]			
99% MeOH (C_S in 2.0)	0.01 M HCl	1.55	1.8
90% MeOH	Res	1.2	0.3
(C_S in 0.6)	0.115 M $HClO_4$	1.4	0.3
	Neutral	0.6	0.3–0.4

[a] C_S in = 0.23. [b] C_S in = 0.2. [c] C_S in = 0.18.

Table II. Standard Zero-Order Rates of Hydrogenation with 3% Pd/C

Solvent	Acidity	Rate, mmol H_2/min	C_S lim
A. Substrate Nitrobenzene, 0.5 mg Pd: C_S in = 0.39			
90% MeOH	0.46 M $HClO_4$	1.0	0.32
75% MeOH	0.46 M $HClO_4$	0.99	0.06
75% MeOH	Neutral	0.8	0.26
65% MeOH	Res	0.35	0.05
B. Substrate Acetophenone, 5 mg of 3% Pd/C, C_S in = 1.3			
99% MeOH	Res	1.66	0.85
90% MeOH	0.23 M $HClO_4$	1.6	0.96
90% MeOH	Neutral	1.1	
75% MeOH	0.23 M $HClO_4$	1.07	0.76
75% MeOH	Res	1.09	0.94
75% MeOH	Neutral	0.6	
C. Substrate Benzaldehyde, 3 mg of 3% Pd/C, C_S in = 2.0			
90% MeOH	0.23 M $HClO_4$	1.63	1.5
90% MeOH	Neutral	0.6	
85% Me_2CHOH	Res	1.77	1.45
80% MeOH	0.23 M $HClO_4$	1.64	<1.0
D. Substrate Benzyl Alcohol, 5 mg of 3% Pd/C, C_S in = 1.94			
90% MeOH	0.46 M $HClO_4$	2.8	1.6
90% MeOH	0.23 M $HClO_4$	2.2	1.8
90% MeOH	0.115 M $HClO_4$	2.1	1.8
90% MeOH	0.046 M $HClO_4$	1.7	1.8
90% MeOH	Res	1.07	1.8
90% MeOH	Neutral	0.05?	
80% MeOH	0.23 M $HClO_4$	1.7	1.75
75% HAc	0.23 M $HClO_4$	2.1	1.7
75% HAc	Res	1.01	1.75
E. Substrate Benzyl Methyl Ether, 5 mg of 3% Pd/C, C_S in = 1.58			
80% MeOH	0.46 M $HClO_4$	0.55	?
80% MeOH	0.23 M $HClO_4$	0.45	?
80% MeOH	Neutral	0.1	?
75% HAc	0.46 M $HClO_4$	1.4	1.4
75% HAc	0.23 M $HClO_4$	1.4	1.4
75% HAc	0.115 M $HClO_4$	1.3	1.4
75% HAc	Res	0.63	1.4
F. Substrate Benzyl Isopropyl Ether, 5 mg of 3% Pd/C, C_S in = 0.86			
80% MeOH	0.23 M $HClO_4$	0.53	?
80% MeOH	Neutral	~0.1	?
75% HAc	0.46 M $HClO_4$	1.5	0.7
75% HAc	0.23 M $HClO_4$	1.3	0.7
75% HAc	0.115 M $HClO_4$	1.3	0.7
75% HAc	Res	0.7	0.7
G. Substrate Cyclohexene, 0.5 mg of 3% Pd/C in 90% MeOH, C_S in = 0.6			
	0.23 M $HClO_4$	0.7	~0.4
	0.023 M $HClO_4$	0.73	~0.4
	Res	0.78	~0.4
	Neutral	0.6	~0.4

catalyst (in Emmett's case 5 mg or less as a rule). Actually the amount of catalyst consistent with useful rates depends on the substrate and is presumably a function of the hydrogen demand. A more rigid limitation applies to the present work, that the rate must be such as not to exceed the capacity of the cooling system. In practice, it was desirable that hydrogen absorption should not exceed 2.5 mmol/min or, in a standard run, be less than 0.5–0.6 mmol/min (this level was such that a half-poisoning rate could be determined without excessive error). After exploratory experiments, 1 mg of Pt (ca. 5 × 10^{-6} atom) was chosen as the standard quantity for reductions of nitrobenzene and cyclohexene and 10 mg for acetophenone. The corresponding amounts of Pd were 0.5 and 5 mg. The latter quantity was also used with benzyl alcohol and 3 mg with benzaldehyde. With rhodium 5 mg was convenient for reductions of benzene, nitrobenzene, and acetophenone, 0.1 mg for cyclohexene.

Results and Discussion

Data on the effects of acidity and variation of solvents with the various substrates and catalysts are shown in Tables I–III. Data on the effects of carrier metal ratios, mainly with standard solvent and acidity, are presented in Tables V–VII. Metallized graphites were studied chiefly in the faster reductions because the high ratio of carrier to metal required becomes inconvenient with larger amounts of metal. The operations with rhodium were less extensive than would be desirable. This work was done last, and the time available to the author was limited.

The notation Res in the acidity columns indicates that the acid present was that resultant from the preparation of the catalyst. This amounted to an initial acid concentration in batches of 10 mg of platinum of 0.016 M and ¹⁄₁₀ that in 1-mg batches. A 5-mg batch of palladium catalyst would have a res acidity of 6.8 × 10^{-3} whereas res for a 0.1-mg batch of rhodium was 0.003. These quantities, while small,

Table III. Standard Zero-Order Rates for Hydrogenation by Rh/C

Catalyst	Solvent	Acidity	Rate, mmol H_2/min	C_S lim
A. Substrate Cyclohexene, 0.1 mg Rh/C (1%), C_S in = 0.6				
	90% MeOH	Res	2.29	0.28
	90% MeOH	0.023 M $HClO_4$	2.16 ± 0.08	0.16
	90% MeOH	2.2×10^{-3} OH	2.4	0.41
	90% MeOH	10^{-2} OH	1.83	0.48
B. Substrate Acetophenone, 5 mg of Rh, C_S in = 1.7				
E	90% MeOH	Neutral	0.97	1.6?
E	90% MeOH	0.03 M HCl	0.73	1.6?
E	75% MeOH	Neutral	0.77	1.58
5% Rh/C	90% MeOH	Res	0.5	1.6?
5% Rh/C	90% MeOH	0.23 M $HClO_4$	0.42	?
1% Rh/C	90% MeOH	0.23 M $HClO_4$	0.22	?
C. Substrate Benzene, C_S in = 1.97				
E	90% MeOH	None	2.05	~1.9
E	85% MeOH	None	1.8	~1.9
E	80% MeOH	None	1.45	~1.5
E	80% MeOH	0.23 M $HClO_4$	1.33	~1.8
E	90% HAc	None	1.1	~1.9
E	85% MeOH	0.003 M HCl	1.06	~1.9
E	85% MeOH	0.02 M NaCl	1.075	~1.9
5% Rh/C	85% MeOH	Res	1.05	~1.9
5% Rh/C	85% MeOH (Cl free)	0.4 M $HClO_4$	1.1	~1.9
5% Rh/C	85% MeOH (Cl free)	0.4 M $NaClO_4$	0.98	~1.9
D. Substrate Nitrobenzene, 5 mg of Rh, 75% MeOH, C_S in = 0.39				
1% Rh/C		0.46 M $HClO_4$	0.84	0.32
3% Rh/C		0.46 M $HClO_4$	0.76	0.34
5% Rh/C		0.46 M $HClO_4$	0.79	0.31
3% Rh/C		Neutral	0.39	?
3% Rh/C		0.01 M OH	0.7 (1.1–0.5)[a]	
E		0.46 M $HClO_4$	0.99 (1.5–0.7)[b]	
E		Neutral	0.98 (1.4–0.7)[c]	
E		0.01 M OH	1.8	0.31

[a] Average of standing 6 min. [b] Average of two nearly identical runs. The figures given are for the first 5 min. The average of the next 6 min was 0.55. [c] Average of first 5 min. Average of next 6 min was 0.53.

are in excess of the amounts strongly adsorbed by the catalysts.

With platinum, the presence or absence of this adsorbed acid is the dominant factor in the influence of acidity on the reduction rate. In the study of nitrobenzene reductions, this factor was ignored initially since it was supposed that the aniline formed would remove adsorbed acid within the first minute or two. Anomalous poisoning results with anions led to the realization that this assumption was unsound, and it is to be noted that there is a large difference between neutral and residual acid rates in the less aqueous solutions (Table IA).

The quantitative aspects of this adsorption of acid were examined with 10-mg batches of Pt/C in the reduction of acetophenone, data being presented in Table IV. In these experiments, after preparation of the catalyst, the quantities of sodium acetate or of alkali given in the first column were added. The solution was then diluted with methanol to 350 ml, equilibrated, and allowed to settle. After removal of supernatant to 10 ml, 30 ml of methanol and 10 ml of acetophenone were added after which the reductions were run. Immediate titration in situ after preparation of catalyst required 0.78 ml of 1 M NaOH, but titration of the supernatant removed in the first experiment required only 0.45 ml. In a parallel experiment with the same amount of acid but only carrier present, there was no significant retention of acid.[24] The amount of acid retained by Pd/C is about half of that held by Pt/C while Rh/C adsorbs still less. Probably corresponding to this, the effect of acidity on rate with Pd/C is marked only with acetophenone, benzaldehyde, and the benzyl–oxygen substrates while with Rh/C acidity is usually inhibitory.

Further increase in acidity through the addition of perchloric or sulfuric acid[25] accelerated the reduction of nitrobenzene moderately but had a more marked effect on C_s lim. Presumably this identifies a case of product inhibition. In 75% methanol with 0.46 M acid, all the aniline that can be formed is protonated, and the zero-order rate continues until more than half of the charge has been reduced. In the absence of added acid, the zero-order rate begins to fade when the reduction is a little more than a quarter done. In other words, when the aniline is 0.11 M, it *begins* to compete for the catalyst surface with 0.28 M nitrobenzene. The effect of added HCl on C_s lim is essentially the same as that of the preferred acids, but the rate is lowered, apparently through toxic action by chloride ion.[26] This subject is discussed further in the following communication. The inhibitory effect of sodium chloride is comparable to that of chloride from HCl but is not compensated by increased acidity. Thus, in 65% methanol sodium chloride inhibited hydrogenation, but HCl did not. The neutral salt also lowered C_s lim presumably by increasing the activity of nitrobenzene more than that of aniline.[27]

In the more aqueous solutions, product inhibition was imperceptible; aniline being relatively soluble in water, the increase in water content raises the activity of nitrobenzene

Table IV. 10 ml of PhCOMe, 40 ml of 99% MeOH, 10 mg of Pt on 200 mg of Charcoal

NaAc added before washout, mmol	HCl remaining before washout, mmol	Rate, mmol H_2/min
None	0.77	1.9
0.4	0.37	1.83
0.48	0.29	1.1
0.56	0.21	0.95
0.64	0.13	0.7
0.68	0.09	0.7
0.77 (NaOH)	Zero	0.7

Table V. Carrier–Metal Ratios for Reduction by Pt, Nitrobenzene in 75% MeOH, 0.46 M $HClO_4$

(Metal × 100)/ carrier	Pt/C "Old" Darco rate	"New" Darco rate	(Metal × 100)/ carrier	Graphite rate
10	0.92			
5	1.6	1.35	0.5	1.15
4		1.47		
3		1.55		
2	1.85	1.65		
1	2.0	1.75	0.1	1.4
0.5	2.2	1.7	0.05	1.72
0.33	2.0	1.73		
0.2		1.6	0.02	1.9
0.1	0.76			
	Pt/C (Z)			
10		0.83		
5		1.33	0.5	0.3
3		1.49	0.2	0.95
1		1.74	0.1	2.29
0.5		1.67	0.05	1.67

Substrate: Cyclohexene in 90% MeOH, 1 mg of Pt (Pt/C B)

	"New" Darco 0.115 M $HClO_4$	Res Acid
5	1.34	1.13
3	1.4	1.2
2	1.45	1.15
1	1.6	1.15
0.5	1.6	

Table VI. Carrier–Metal Ratios for Reduction by Pd

Pd/C Metal × 100/ carrier	Rate	Pd/graphite Metal × 100/ carrier	Rate
Nitrobenzene: 0.5 mg Pd in 75% MeOH, 0.46 M $HClO_4$			
9	0.85	0.02–0.05	2.1
1–5	1.0	0.01	1.4
Benzyl Alcohol: 5 mg of Pd in 90% MeOH, 0.23 M $HClO_4$			
10	1.8	0.5	1.9
1–5	2.1	0.2	1.5

Table VII. Carrier–Metal Ratios with Rh/C

"New" Darco Metal × 100/carrier	Rate
6	(0.3)[a]
4	(0.8)[a]
2	(1.2)[a]
5 (cat. E)	2.36[b]
1	2.16[c]
0.6	2.4
0.33	2.3
0.16	1.0

		Graphite[d]	
Metal × 100/carrier	Rate	Metal × 100/ carrier	Rate
Benzene, 5.0 mg of Rh in 85% MeOH			
5 (cat. E, neutral)	1.8		
5	1.05[d]	0.5	1.1
1	0.5[d]	0.3	1.45
5 (E, neutral)	1.45[e]	0.25	1.5
5	0.7[d,e]	0.1	0.5
3	0.53[d,e]		
1	0.4[d,e]		

[a] Run on inferior cyclohexene. Result should be multiplied by ~$^3/_2$. [b] 0.25 mg of Rh. [c] Average of five runs varying between 2.08 and 2.24. [d] Res acid present = 0.03 M HCl. [e] In 80% MeOH.

selectively. In agreement with this, added acid had no effect on C_s lim in 65 and 60% methanol, though it increased the rate.

Whereas in methanolic solutions throughout this study, *the rate increased with increasing methanol content* (up to 95%) in acetic acid solutions maximal rates were in the neighborhood of 75% acetic acid (or of a hypothetical hydrate). In these acetic acid solutions the effects of added perchloric and hydrochloric acids on the rate were similar to their effects in methanol, but the C_s lim was unaffected. The solvent itself sufficed to bind the aniline formed.

These studies with nitrobenzene appear to support rather thoroughly the arguments on the effect of solvents stated in the introduction. Beyond checks on the validity of these principles, it was not felt necessary to make further examinations in detail. Solvent variation in reductions of cyclohexene, benzene, and benzyl alcohol was, in any case, restricted by the properties of the reduction products.

With acetophenone and cyclohexene (Tables IB and IC) as substrates, the effect of acid on the activity of platinized charcoal was much the same as above if we take into account the point that acid is now irrelevant to product inhibition (probably not significant anyway).

The palladized charcoal reductions of nitrobenzene and cyclohexene (Tables IIA and IIG) were relatively insensitive to acid in respect to rate, whereas the substrates possessing a C–O bond are highly sensitive. The extreme case is benzyl alcohol whose hydrogenation rate is almost entirely acid dependent leading to the hypothesis that it is the protonated species that is being reduced.[28] The benzyl ethers were also highly sensitive to the *presence* but were less so to the concentration of acid. Their reduction rates in neutral solution were low but appreciably higher than that of benzyl alcohol and clearly distinguishable from zero. The reduction rates of these ethers were lower than that of benzyl alcohol (except in neutral solution) but did not differ significantly from each other. The less water soluble ether had a lower value of C_s lim as would be expected.

The function C_s lim was appreciably lower in acetophenone reductions catalyzed by Pd/C than with Pt/C, permitting use of a smaller charge. On the other hand, cyclohexene was adsorbed less strongly on Pd.

The reductions of cyclohexene, acetophenone, benzene, and nitrobenzene by rhodium on carbon were examined. Benzaldehyde, as reported by Dunworth and Nord,[29] is reduced slowly, in fact, very much more slowly than by palladized charcoal. The neutral rate with acetophenone is not far below that with palladium, but acid inhibits this catalyst with acetophenone as with benzene. The reduction of cyclohexene was little affected by acid and that of nitrobenzene was promoted, as also by alkali.[28] The reduction of nitrobenzene by Rh/C is very slow as compared to that by palladium or platinum while the ability of Rh/C to reduce aromatic rings is one of its special recommendations. It is not clear to what extent this is a matter of adsorption. Nitrobenzene is clearly rather poorly adsorbed on rhodium, as shown by the high value of C_s lim. Benzene is not very strongly adsorbed but may be more strongly than on platinum. (Since Pt/C does not reduce benzene, comparison by C_s lim is impossible.)

Dunworth and Nord[29] had remarked on the exceptional activity of Rh/C in the reduction of unsaturated fatty acids with isolated double bonds. They reported activity about twice that of Pd/C but studied only a 5% catalyst that may have resembled catalyst E. The activities presented in Tables IIIA and VII are the highest observed in this study, and the turnover rate compares favorably with those reported for enzymes.[30] This reduction is also peculiar in that, while the rate is little affected by acid and is slightly promoted by alkali in low concentration (but inhibited in higher), the C_s lim is markedly dependent on the acidity.

These disparate effects of acidity and alkalinity between these three catalytic metals and among the various substrates suggest that the fine details of catalytic hydrogenation may vary markedly from case to case.

The Metal–Carrier Ratio. Two samples of charcoal (Darco) were used which were not quite equivalent as carriers. Roughly a 3% Pt/C with the newer charcoal was considered comparable to a 5% with the older. Two methods of preparation were used, differing in that one (B) employed a trace of Pd to initiate deposition of metal while the other (Z) did not. With the new charcoal, the two methods gave very similar preparations, maximal activity being at about the 1% catalyst. The "old" charcoal gave a somewhat higher maximal activity in the range of 100–300 parts of carrier to 1 of metal. The platinized graphites required much more carrier with some variation according to the method of preparation. Pt/graphite (B) was not pushed to a point of diminishing activity with increased amount of carrier. The difficulty of handling the rather large amounts of solid in the small amount of aqueous solution desired imposed a limit of convenient operation. (This was still more forcing when larger amounts of metal would be needed.)

With palladium, the carrier–metal ratio was less critical; no significant differences were observed in the reduction of nitrobenzene from 1% catalyst to 5% catalyst. Curiously, the palladized graphite was markedly more active for this purpose than palladized charcoal.

Against benzyl alcohol as substrate, palladized charcoal was almost as efficient as 10% catalyst as in the range 1–5%. The palladized graphites were slightly less active, but the range of composition was not thoroughly explored.

The situation with rhodium is complicated by unknown facts as the manufacturers of catalyst E have consistently refused to divulge any information as to the preparation of their catalysts.[31] Consequently, it is impossible to correlate the properties with the method of formation. As compared to the Rh/C prepared in this laboratory, catalyst E was clearly superior for reduction of benzene and acetophenone, clearly inferior against cyclohexene, and extremely erratic against nitrobenzene.

Against cyclohexene, maximal efficiency lay in the range of 0.3–1% catalysts. Against benzene a higher ratio of metal to carrier (ca. 5%) was more effective. Catalyst E was more effective than the Rh/C prepared immediately before reductions. The difference appeared to be due in part to the inhibitory effect of acidity and chloride ion; however, the data in Table IIIB did not reconcile the disparities entirely. Rhodium on graphite was very nearly as effective as catalyst E and maximal activity here lay in the region of 0.25–0.3% catalysts.

Catalyst E was also superior to those prepared in this laboratory in the reduction of acetophenone. A 5% catalyst was more effective than a 1% preparation.

In the reduction of nitrobenzene, there was little variation in the catalysts prepared here from 1% to 5%. Catalyst E gave a high rate in the presence of alkali, but in acid and neutral conditions started out with a high activity which was halved within 5 min. The function C_s lim is rather high in this reduction (corresponding to relatively poor adsorption of nitrobenzene on rhodium), but that alone cannot account for this behavior which was observed in the catalysts prepared here *only* in the presence of alkali. The results suggest that the rhodium deposits are subject to alteration in the early stages of the reduction of nitrobenzene.

While the original hypothesis as to the graphitic nature of the charcoal surface seems to be tolerably borne out, it is evident that quite minor variations in the charcoal may be responsible for considerable variation.

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Registry No.—Platinum, 7440-06-4; palladium, 7440-05-3; rhodium, 7440-16-6; nitrobenzene, 98-95-3; acetophenone, 98-86-2; cyclohexene, 110-83-8; benzaldehyde, 100-52-7; benzyl alcohol, 100-51-6; benzyl methyl ether, 538-86-3; benzyl isopropyl ether, 937-54-2; benzene, 71-43-2.

References and Notes

(1) This investigation was supported in part by funds from the Public Health Service Research Grant CA-08748 from the National Cancer Institute.

(2) Some years ago, at the suggestion of Mr. Emil Lorz, palladized and platinized graphites were prepared. These catalysts resembled qualitatively the corresponding metallized charcoals. Since ordinary charcoals are known to be extensively graphitic in structure, it seemed probable that metallized charcoals are essentially metallized graphites. A nongraphitic charcoal prepared by the reaction of sodium with hexachlorobenzene [J. Gibson, M. Holohan, and H. L. Riley, *J. Chem. Soc.*, 456 (1956)] afforded catalysts of minimal activity.

(3) (a) H. C. Yao and P. H. Emmett, *J. Am. Chem. Soc.*, **81**, 4125 (1959); (b) *ibid.*, **83**, 796 (1961).

(4) (a) A. S. Hussey, G. W. Keulks, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, **33**, 610 (1968); (b) A. S. Hussey and G. P. Nowack, *ibid.*, **34**, 439 (1969).

(5) Equation 1 is equivalent to eq 1 of Yao and Emmett.[3a] Most of the real differences in the kinetic treatment of the present and the above-cited papers are in the evaluation of the θ factors.

(6) A further question which is not readily answered is whether hydrogen and substrate are adsorbed independently or competitively. For palladium on alumina, Hussey and Nowack[4b] incline toward independent adsorption, and the data of the present work are consistent with this. For indications that, taken together, suggest the contrary, cf. E. B. Maxted and H. C. Evans, *J. Chem. Soc.*, 1750 (1939); E. B. Maxted and G. T. Ball, *ibid.*, 2778 (1954).

(7) Yao and Emmett[3] take β as 1. The actual value of β is irrelevant to the present discussion as long as it is small.

(8) In the presence of poison, the term $\alpha_i C_i$ is relatively large and θ_s must diminish with C_s. However, by operating above the C_s lim in unpoisoned situations, it is possible to observe a reasonably linear reduction rate for a long enough period to render extrapolation to zero time unnecessary.

(9) A considerable amount of exploratory work was done with dimethyl maleate, maleic acid, and cinnamic acid. These substrates were abandoned when it was found that acetic ion was a weak inhibitor and probably other anions of carboxylic acids. There was also some concern that in alcoholic–aqueous solutions the nature of the substrate could change, especially if esterifications should be catalyzed on the active surface.

(10) Dr. Robert Klein of this Institute had experienced difficulty in completing the debenzylation of some methylpentoside 3,5-dibenzyl ethers. It later became apparent that poisoning (presumably originating in the benzyl chloride used in synthesis) was involved. The rates of hydrogenolysis of the mono- and dibenzyl sugars appear to have been in a ratio of about 1:3 which could be a function of adsorption coefficients. If only the ring, the methylene, and the O need lie on the catalyst surface, it would seem that the other O-bound structure must be very bulky to interfere, unless it bears another point of attachment.

(11) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 137, 146 (1936), give 28.6 and 49.8 kcal/mol for the reduction of cyclohexene and benzene at 80 °C.

(12) The small samples (2 and 3 ml, respectively) of nitrobenzene and cyclohexene were added after the temperature had been set.

(13) The effect of a 1 °C variation in temperature on rate varies from substrate to substrate. For cyclohexene, Hussey et al.[4a] give a rather low energy of activation, 6–7 kcal/mol. This leads to a temperature effect

for 1 °C less than other uncertainties. Yao and Emmett[3a] give 13–14 kcal/mol for the energy of activation in the reduction of nitrobenzene. According to that figure, an increase in temperature of 1 °C should produce a rate increase of about 8%. No figures are available for the other substrates used. One suspects that the energy of activation for hydrogenation of benzene may be relatively high.

(14) W. T. Olson, H. F. Hipscher, C. F. Buess, I. A. Goodman, I. Hart, J. M. Lamneck, Jr., and L. C. Gibbons, *J. Am. Chem. Soc.*, **69**, 2451 (1947).

(15) Since the acetophenone reductions were not run near to completion, it was possible and convenient to recover substrate after filtration from catalyst, a number of batches being combined. Control runs were made on all batches, recovered or new, before use.

(16) Commercial acetophenone could also be purified by repeated passages through Raney nickel columns, followed by distillation. This process had no advantage over synthesis. Aside from the complications of handling very large amounts of substrate in solutions, the adsorption is not very efficient. E. B. Maxted [*J. Chem. Soc.*, 624 (1947)] considered thiophene a relatively weak poison which acts mainly through reduction to tetrahydrothiophene. Under nonreducing conditions, the inhibitor competes poorly with the much larger amount of substrate. An attempt at a similar column purification of benzyl methyl ether was unsuccessful.

(17) $C_{i\,1/2}$ is the concentration of poison that lowers the reduction rate to half the standard value.

(18) Darco G-60 was used. In the earlier part of this work, the sample was a special one obtained from the manufacturer (Darco Department, Atlas Powder Co.) and prepared by the method in use when the author first employed this method (ca. 1940). A later sample, here called "New Darco," was the usual commercial grade of the present time.

(19) The method of E. Ott and R. Schröter, *Ber.*, **60**, 624 (1927).

(20) R. Baltzly, *J. Am. Chem. Soc.*, **74**, 4586 (1952).

(21) H. I. Zeliger, *J. Catal.*, **7**, 198 (1967).

(22) Zeliger reported that chloroplatinic acid was reduced by hydrogen and platinum deposited on finely divided carriers *wetted* by the solution. This does not appear to have been investigated previously since it was "known" that hydrogen did not precipitate metal from chloroplatinic acid solutions.

(23) Hussey and co-workers[4a] reported acetic acid to have been unusable in their studies. This may correspond to the greater precision of their operations or the acetic acid modifying the nature of their support (activated alumina).

(24) That such an adsorption of acid exists has been suspected but not demonstrated previously. Cf. ref 20.

(25) Perchloric acid was preferred. The sulfuric acid available gave consistently *lower* rates for about the first 5 min of reductions. It is suspected that traces of nitrous or nitric acid were present which acted initially as poisons but were then reduced to ammonia which would have been nontoxic under the conditions.

(26) Cf. M. Freifelder, "Practical Catalytic Hydrogenation", Wiley-Interscience, New York, N.Y., 1971, p 26. Freifelder appears to be the first to suspect this inhibitory action, which, however, he believed confined to nonaqueous solutions.

(27) Phosphoric and oxalic acids were intermediate between perchloric and hydrochloric. The oxalic acid may have produced some inhibition as its anion.

(28) That a significant amount of $BzOH_2^+$ is present is suggested by the observation that when the charge of benzyl alcohol was added to the solvent containing perchloric acid the temperature of the solution rose about 2 °C. When acid was absent, a fall in temperature of about the same size was noted. These temperature effects were not observed with the benzyl ethers.

(29) W. P. Dunworth and F. F. Nord, *J. Am. Chem. Soc.*, **74**, 1459 (1952).

(30) The rates of 2–2.4 mmol/min per 0.1 mg of Rh give turnover rates of about 2×10^3 mol atom^{-1} min^{-1}: reported for invertase, 4×10^3, carboxylase, 10^3, choline esterase and catalase, ca. 10^6. The figure of 2×10^3 is, of course, based on the number of Rh atoms on the catalyst sample, whereas the enzyme figures are per active site, usually one to a molecule. If one assumes that the metal plaques average five atoms thick and that an adsorbed molecule of cyclohexene obscures the surface of four atoms of Rh, the turnover rate becomes 4×10^4.

(31) Specifically they were asked whether they employed (a) reduction by hydrogen, (b) chemical reduction, or (c) ignition of carrier impregnated with metal salt. (All these methods have been employed in the past for one catalyst or another.) They were also asked what charcoal they use.

Studies on Catalytic Hydrogenation. II. Poisoning by Nucleophiles[1]

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A selected group of nucleophilic inhibitors has been studied in the reduction of different types of substrates and with platinum, palladium, and rhodium on carbon catalysts. Variation of solvent affects the adsorption of inhibitors along the same lines as with substrates. Higher molecular inhibitors, having high intrinsic toxicity through obstructing access to an extended surface, also show diminished adsorption coefficients. Certain irregularities in poisoning tendencies may be due to differing details of hydrogenation of different substrates.

The extensive investigations of catalyst poisoning by Maxted[3] permit a division of poisons into two main classes,[4] those attaching themselves to the catalyst through an unshared electron pair, and a second group of metallic cations—the subject of the third communication of this series.

Poisons of the first class are acting as nucleophiles and a logical extension of the original concept led to the recognition of bases and of iodide ion as poisons. Weaker nucleophiles such as chloride,[5] bromide, and acetate (or carboxylate ions, generally) have not usually been recognized as inhibitors in default of specific investigation. Two major questions left unanswered by Maxted's work were:

1. To what extent are his generalizations, based mainly on the study of Willstätter platinum and, to a lesser degree, of a supported nickel catalyst, valid for hydrogenation catalysts in general?

2. To what extent are toxicities altered by comparison with different substrates and by changes in solvent?

It seemed worthwhile, therefore, to attempt a study using several metallized charcoals with some variation of substrates and of solvent conditions and a representative group of poisons, though not the very large selection examined by Maxted.

In the preceding communication, the effect of solvent conditions on reaction rate has been considered, and it has been shown that under suitable conditions the rate may be of zero order in respect to hydrogen pressure and substrate concentration: i.e., the adsorption terms approximate the value of 1. Under such conditions, presence of poison should modify the substrate adsorption term (θ_s) so that

$$\theta_s = \frac{\alpha_s C_s}{\alpha_s C_s + \alpha_i C_i} \qquad (1)^6$$

and at half-poisoning, $\theta_s = \frac{1}{2}$ and $\alpha_i C_i = \alpha_s C_s$.

Plots of rate against poison concentration according to eq 1 with $C_{i\,1/2}$ as the unit of poison concentration give theoretical poisoning curves such as curve A of Figure 1. The characteristic feature of such a curve is that at $C_i = 2C_{i\,1/2}$ the rate should be one-third of the standard and at $C_i = \frac{1}{2}C_{i\,1/2}$, two-thirds. (Obviously, other simple relationships are also deducible.) On this basis in a poisoning study, one