[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

Homogeneous Hydrogenation in the Absence of Transition-Metal Catalysts[1]

BY CHEVES WALLING AND LASZLO BOLLYKY[2]

RECEIVED APRIL 20, 1964

The possibility of bringing about reaction of molecular hydrogen with organic substrates has been investigated in homogeneous media under conditions of simple acid–base catalysis and in the presence of free-radical intermediates. The homogeneous hydrogenation of benzophenone to benzhydrol occurs in the presence of potassium *t*-butoxide at 130–200° and approximately 100-atm. H_2 pressure, presumably *via* a hydride ion intermediate. Cyclohexane–$AlBr_3$–HBr systems absorb H_2 at 90–140° to give complex mixtures of saturated products including cyclohexane and methylcyclopentane, presumably *via* hydride transfer from hydrogen to carbonium ions. Hydrogen at 100-atm. pressure has no significant effect on the rate or products of benzoyl peroxide decomposition in chlorobenzene.

Although the reaction of molecular hydrogen with unsaturated organic molecules is generally energetically feasible, a potential barrier to the process exists which is usually overcome by the use of heterogeneous catalysts or certain transition metal catalysts in homogeneous systems.[3] The purpose of the work reported here has been to investigate the possibility of homogeneous hydrogenation *via* simple acid–base catalysis (admittedly under rather drastic conditions) and by means of free-radical intermediates.

Base Catalysis.—Two groups of observations of long standing in the literature suggest that simple base catalysis of homogeneous hydrogenation might be achieved in suitable systems. The first of these is the base-catalyzed exchange between D_2 and water,[4] which is pictured most easily in terms of the (highly unfavorable) equilibrium

$$H_2 + OH^- \rightleftharpoons H^- + H_2O \qquad (1)$$

a formulation supported by both kinetic measurement[5] and kinetic isotope effects.[6]

Second, a considerable number of reactions are known in which treatment of organic molecules with strong bases at elevated temperatures leads to oxidation with evolution of molecular hydrogen. Perhaps the oldest is the Varrentrapp reaction in which caustic fusion of oleic acid produces hydrogen, palmitic acid, and acetic acid.[7] Since at least one step in these processes involves dehydrogenation, they may be considered as simply the back reactions of base-catalyzed hydrogenations which might conceivably reverse under suitable conditions.

From the foregoing, a scheme for base-catalyzed hydrogenation might be

$$RO^- + H_2 \rightleftharpoons ROH + H^- \qquad (2)$$

$$H^- + R_2C{=}O \rightleftharpoons R_2CH{-}O^- \qquad (3)$$

$$R_2CHO^- + ROH \rightleftharpoons R_2CHOH + RO^- \qquad (4)$$

in which (3) is simply nucleophilic attack by hydride on a suitably polarized double bond. Since step 2 is certainly the most unfavorable equilibrium, very strong base would probably be required.[8]

For our initial studies we chose potassium *t*-butoxide in *t*-butyl alcohol as our basic media, and benzophenone as a substrate resistant to strong base and high temperatures, but which should still be susceptible to hydride ion attack. Results of a series of experiments are shown in Table I, where we see that hydrogen uptake and reduction to benzhydrol occurs at temperatures of 150–200° under approximately 100-atm. hydrogen pressure. Experiments were carried out in a stirred nickel-lined autoclave, but any catalytic effect of nickel was ruled out by a parallel experiment essentially equivalent to run 2, using a Teflon liner and Teflon-clad stirrer where reduction was also observed. Unless indicated, no further reduction to diphenylmethane took place and no other products (other than recovered benzophenone) were detected. Table I serves to establish the general limits of reaction conditions. At low catalyst concentrations in *t*-butyl alcohol reduction is slow below 200° (runs 2–4), but becomes rapid even at 150° with excess base (run 5). Reduction also occurs in benzene, and the most effective solvent appears to be diglyme (the dimethyl ether of diethylene glycol) where, with excess base,

TABLE I

BASE-CATALYZED REDUCTIONS OF BENZOPHENONE

Benzophenone 0.43–0.46 *M* unless indicated

No.	Solvent	Catalyst	Mole/l.	H_2, atm.	Temp., °C.	Time, hr.	Benzhydrol, %
1	*t*-BuOH	None		102	170	28	0
2	*t*-BuOH	*t*-BuOK	0.093	135	210	25	98
3	*t*-BuOH	*t*-BuOK	.086	102	170	18	63
4	*t*-BuOH	*t*-BuOK	.093	102	153	50.5	47
5[a]	*t*-BuOH	*t*-BuOK	.333	96	150	14.5	98
6	Benzene	*t*-BuOK	.093	125	204	23	98
7	Diglyme	*t*-BuOK	.093	100	170	18	52
8[b]	Diglyme	*t*-BuOK	.283	78	130	5	98
9	*t*-BuOH	*t*-BuOLi	.086	102	170	18	32
10	Benzene	*t*-BuONa	.464	95	100	5	0
11	H_2O	KOH	8.9	125	200	28	1
12	H_2O	KOH	8.9	110	220	220	13.3[c]
13	Diglyme	$(i\text{-Pro})_3Al$	0.093	123	210	34	Trace[d]
14	Diglyme	$(i\text{-PrO})_3Al$	.093	110	140	34	8.4[d]
15	Diglyme	$(i\text{-PrO})_3Al$	.093	102	145	216	13.1[d]

[a] Benzophenone, 0.111 *M*. [b] Benzophenone 0.094 *M*. [c] Plus a trace (<2%) of diphenylmethane. [d] Probably caused chiefly by Meerwein–Pondorf reduction; see Experimental.

(1) Taken from the Ph.D. Thesis of L. Bollyky, Columbia University, 1963. Partial support of this work by a grant from the National Science Foundation is gratefully acknowledged. A preliminary report has been published: C. Walling and L. Bollyky, *J. Am. Chem. Soc.*, **83**, 2968 (1961).

(2) American Cyanamid Fellow, 1962–1963.

(3) For review and discussion, *cf.* J. Halpern, *Advan. Catalysis*, **11**, 301 (1959).

(4) K. Wirtz and K. F. Bonhoeffer, *Z. physik. Chem.*, **177A**, 1 (1936); W. K. Wilmarth, J. C. Dayton, and J. M. Fluornoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953); S. L. Miller and D. Rittenberg, *ibid.*, **80**, 64 (1958).

(5) J. M. Fluornoy and W. K. Wilmarth, *ibid.*, **83**, 2257 (1961).

(6) Y. Pocker, *Chem. Ind.* (London), 1383 (1959).

(7) F. Varrentrapp, *Liebig's Ann.*, **35**, 196 (1840). For more recent work and studies of reaction mechanism, *cf.* R. G. Ackman, P. Linstead, B. J. Wakefield, and B. C. L. Weedon, *Tetrahedron*, **8**, 221 (1960); W. A. Bonner and R. T. Rewick, *J. Am. Chem. Soc.*, **84**, 2334 (1962).

(8) The fairly easy hydrogenolysis of organometallic compounds presumably involves attack on hydrogen by the very strongly basic carbanion or carbanionoid reagent, in a manner analogous to (2). For examples, *cf.* K. Clauss and H. Bestian, *Ann.*, **654**, 8 (1962); F. L. Ramp, E. J. DeWitt, and L. E. Trapasso, *J. Org. Chem.*, **27**, 4368 (1962).

reduction was complete in 5 hr. at 130°. Diglyme belongs to the group of solvents in which bases are unusually strong and carbanion reactions rapid,[9] presumably because of cation solvation. Attempts to use even more effective solvents, *e.g.*, hexamethylphosphoramide and dimethyl sulfoxide, were unsuccessful owing to their instability under reaction conditions. With dimethyl sulfoxide a base-catalyzed reaction occurs with benzophenone which we have reported elsewhere.[10]

Table I includes some experiments with other catalysts. Under very drastic conditions, slow reduction is even observed with concentrated aqueous KOH (runs 11–12). Aluminum isopropoxide was tried, in the hope that reduction might occur through a cyclic transition state somewhat like that postulated for the Meerwein–Pondorf reduction,[11] although with essentially negative results. Although not included in the table, no reduction was observed in the presence of tributyl borate or 2-hydroxypyridine, a possible bifunctional catalyst.[12]

Table I indicates that reduction is more rapid at high base:benzophenone ratios. This is further illustrated in Table II where benzophenone concentration was varied at 170° and other quantities held constant. While the data do not permit any kinetic analysis, we believe that the decrease in yield is in part caused by the decrease in basicity of the system as *t*-butoxide is converted to the anion of the stronger acid[13] benzhydrol with a resulting drop in reaction rate.

TABLE II

EFFECT OF BENZOPHENONE:*t*-BuOK RATIO ON RATE OF BASE-CATALYZED HYDROGENATION IN *t*-BuOH AT 170°

All experiments 0.09 *M* base, 102-atm. H_2 pressure, 18-hr. runs, unless noted

Benzophenone:base	Benzhydrol yield, %	Benzophenone:base	Benzhydrol yield, %
0.5	89.0	10.0	26.3
2.5	64.3	10.0	24.3
2.5	67.5	10.0	41.7[a]
5.0	62.7		

[a] 28.65-hr. run.

Finally, we have investigated base-catalyzed hydrogenation of some additional substrates under conditions effective for benzophenone (Table III). No hydrogen uptake was observed with cyclohexene or with acetone which apparently underwent extensive aldol condensations under the experimental conditions. Hydrogen uptake was observed with nitrobenzene, leading to partial reduction to aniline. Only about 4% unreacted nitrobenzene was recovered, and the balance of the products were unidentified brownish black residues.

TABLE III

Substrate, moles/l.	Substrate: base ratio	H_2, atm.	Temp., °C.	Time, hr.	Product, %
Benzophenone, 0.464	5	135	210	25	Benzhydrol (98)
Acetone, 5.0	20	148	170	24	None[a]
Nitrobenzene, 0.464	5	118	175	23	Aniline (32)[b]
Cyclohexene, 1.44	17.5	130	190	30	None[c]

[a] Only aldol products. [b] Recovered nitrobenzene (4%) plus dark solids. [c] Starting material unchanged.

In summary, the occurrence of simple base-catalyzed hydrogenation has been demonstrated, and our results are at least consistent with the sequence of reactions (2–4) involving a hydride ion intermediate. However, the reaction is probably of limited synthetic value, since few substrates are stable under the high temperatures and strongly basic conditions required.

Acid-Catalyzed Hydrogenations.—As we have seen, base catalysis converts molecular hydrogen to a nucleophilic active species (hydride ion) capable of attacking suitable organic substrates. Similarly, the possibility exists of converting the substrate to a reactive electrophilic species capable of attacking the molecular hydrogen, *e.g.*, by a process such as

$$ROH + H^+ \rightleftharpoons R^+ + H_2O \quad (5)$$

$$R^+ + H_2 \rightleftharpoons RH + H^+ \quad (6)$$

Reaction 6 parallels the great variety of known facile hydride ion transfers in organic chemistry,[14] and its feasibility should be determined largely by its energetics. In the gas phase ΔH, calculated from bond dissociation energies and ionization potentials, is approximately 85 kcal. for R = methyl and 155 kcal. for R = *t*-butyl. However, in a polar solvent, the very large solvation energy of H^+ makes reaction more favorable. Thus, in water, taking heats of solvation for H^+ and R^+ as −256 and −80 kcal. (the latter comparable to a halide ion), ΔH becomes −91 kcal. for R = methyl and −21 kcal. for R = *t*-butyl. Considerable evidence that such processes are indeed possible exists in petroleum technology as examples of the modification of carbonium ion reactions by the presence of hydrogen,[15] and the experiments which we have carried out are very preliminary in nature, intended merely to indicate some of the limits of reaction.

Our calculation of energetics suggest that ease of hydrogenation will decrease rapidly with increased carbonium ion stability. In keeping with this prediction, no hydrogen uptake was observed by solutions to triphenylmethyl chloride in either SO_2 or dimethylformamide, or by triphenylcarbinol in sulfuric acid even at temperatures up to 150–180°. Attempted hydrogenation of isobutene and cyclohexene in the presence of $AlCl_3$ dissolved in chloroform gave traces of saturated hydrocarbon at 140°, 120 atm. of H_2, but no significant hydrogen uptake. Marked hydrogen uptake was observed by a 15.8% solution of $AlBr_3$ in cyclohexane at 150° and 82-atm. pressure. The products were completely saturated, but contained 4% methylcyclopentane and 2% cyclohexane together with many higher-boiling products. No reaction was observed at 100°, but hydrogenation could be accomplished at 95° (to give essentially the same mixture of products) by adding *n*-propyl bromide as a source of HBr. Benzene in the presence of $AlBr_3$ showed a

(9) *Cf.*, for example, H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960).

(10) C. Walling and L. Bollyky, *J. Org. Chem.*, **28**, 256 (1963).

(11) R. B. Woodward, N. L. Wendler, and J. F. Brutschy, *J. Am. Chem. Soc.*, **67**, 1425 (1945).

(12) C. G. Swain and J. F. Brown, *ibid.*, **74**, 2538 (1952).

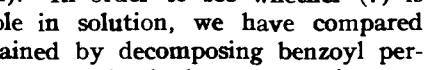
(13) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952); R. West and R. H. Baney, *ibid.*, **81**, 6145 (1959).

(14) As examples, *cf.* P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956); N. C. Deno, N. Friedman, J. D. Hodge, F. P. Mackay, and G. Saines, *ibid.*, **84**, 4713 (1962).

(15) *E.g.*, V. N. Ipatieff and L. Schmerling, *Ind. Eng. Chem.*, **40**, 2354 (1948), have reported the modifying action of hydrogen on the $AlCl_3$-catalyzed isomerization of hydrocarbons.

small hydrogen uptake at 180° and 68-atm. pressure. However, no cyclohexane or methylcyclopentane were detectable among the black, tarry products. Although the study was not carried further, it certainly suggests the feasibility of reaction 6 under suitable conditions.

Radical Attack on Hydrogen.—A radical path for homogeneous hydrogenation does not appear particularly attractive, since the step



$$R\cdot + H_2 \longrightarrow RH + H\cdot \qquad (7)$$

is generally endothermic ($\Delta H = \sim 2$ kcal. even for R = methyl or phenyl). In order to see whether (7) is actually observable in solution, we have compared the products obtained by decomposing benzoyl peroxide in chlorobenzene under hydrogen and nitrogen; Table IV. If (7) occurs, hydrogen should lead to an

TABLE IV

EFFECT OF HYDROGEN ON DECOMPOSITION OF 5% BENZOYL PEROXIDE IN CHLOROBENZENE (22.5 HR. AT 80°)

	Products, %		
Gas (atm.)	Peroxide	Benzene	Benzoic acid
N_2 (1)[a]	5.86	6.35	27.2
H_2 (1)[b]	3.7 ± 1	8.4 ± 1.6	26.4 ± 2
N_2 (102)[c]	12.25 ± 0.05	9.3 ± 0.14	26.8 ± 0.2
H_2 (51–102)[b]	12.15 ± 1.8	11.15 ± 0.9	28.0 ± 1.1

[a] Single experiment. [b] Average of four runs. [c] Average of two runs.

increase in the yield of benzene (or possibly benzoic acid if the benzoyloxy radical can also react with hydrogen). While the results indicate a very small increase in the benzene yield, its significance is marginal and there is certainly no evidence for any very rapid attack on hydrogen comparable, say, to the facile reaction and large change in products observed with carbon monoxide under similar conditions.[16] The presence of hydrogen also has no significant effect on decomposition rate, judged by the amount of unreacted peroxide remaining in the systems.

Experimental

Base-Catalyzed Reactions.—Most experiments were carried out in a stirred 300-ml. stainless steel autoclave (Autoclave Engineers, Inc., Magnadrive), electrically heated, equipped with a nickel (or Teflon) liner and stirrer. For experiments in Table I, benzophenone, solvent, and a stock solution of sublimed potassium *t*-butoxide (or other catalyst) were weighed into the liner in a dry-box, the liner covered with aluminum foil for transfer and immediately placed in the autoclave.

Reaction volumes were approximately 100 ml. After reactions, the products were poured into 150 ml. of water and extracted with ether. The extract was washed and dried; the ether was removed under reduced pressure; g.l.c. analysis showed no products but benzhydrol and benzophenone, and crude material balances were typically 99%. A typical experiment in which reduction was complete yielded 77% recrystallized benzhydrol, m.p. 66–67°, identified by mixture m.p., infrared spectra, and g.l.c. retention time. Quantitative yields were determined by g.l.c. analysis (5% QF-I silicone, 1% Carbowax on firebrick at 165°) by comparing peak areas for benzophenone and benzhydrol with known mixtures.

In experiments using aluminum isopropoxide the solution was held at 80° for 4–8 hr. at reduced pressure (106 mm.) before hydrogenation to remove acetone formed by Meerwein–Pondorf reduction. This reaction led to some reduction of benzophenone so that the small yields reported are probably not evidence for additional hydrogenation.

In the above procedure, heating and cooling the autoclave took several hours, so in the fixed time runs of Table II, procedure was modified in that the autoclave was placed in a preheated oil bath, and, after reaction, the hot oil was removed and replaced by cold for rapid cooling.

Experiments in Table III were carried out similarly to those in Table I. Aniline was isolated by extraction with dilute HCl and was identified by infrared spectra and g.l.c. retention time.

Acid-catalyzed reactions were carried out in the same equipment, using a glass liner and stirrer. Experiments in which no pressure drop was observed were not investigated further. Hydrogenation of a 15.8% solution of $AlBr_3$ in cyclohexene at 150° and 82-atm. H_2 pressure showed a pressure drop of 21 atm. in 26.5 hr. The product consisted of two phases, a light brownish yellow upper layer and a dark waxy lower layer. The upper layer was washed with alkali and water and distilled. Analysis by g.l.c. of the first fractions showed methylcyclopentane and cyclohexane, identified by collection and infrared and n.m.r. spectra. All fractions were completely saturated hydrocarbons from their infrared and n.m.r. spectra and nonreactivity with Br_2 in CCl_4. The lower waxy layer was dissolved in ether and treated similarly to yield again only saturated products by the same tests. The reaction in the presence of propyl bromide (equivalent in amount to the $AlBr_3$) was carried out similarly with essentially identical results except for the lower temperature required.

Decompositions of benzoyl peroxide were crrried out in the same equipment using the glass liner; 5% solutions in chlorobenzene were decomposed as indicated in Table IV. Unreacted peroxide was determined iodometrically, benzene by g.l.c. analysis, and benzoic acid either gravimetrically after extraction with base and reprecipitation, or by titration. The two methods gave good agreement on several samples. As noted, the results in Table IV are averages of several experiments carried out under the same conditions and experimental errors given are the spread of all experiments.

(16) C. Walling and S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).