[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE HYDROGENATION OF BENZENE IN THE PRESENCE OF METALLIC COPPER

BY ROBERT N. PEASE AND R. B. PURDUM

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According to Sabatier and Senderens,[1] copper, as well as some others of the metal hydrogenation catalysts, has no measurable activity in the hydrogenation of benzene, whereas nickel easily catalyzes the reaction. Recent investigations[2] having shown that a copper catalyst can readily be prepared whose activity in the hydrogenation of ethylene is of the same order as that of nickel and is appreciable some 200° below the minimum reaction temperature stated by Sabatier, it appeared that a reinvestigation of the influence of copper on the hydrogenation of benzene was in order.

Should copper, which is highly active toward ethylene-hydrogen mixtures and adsorbs either gas more strongly than it does others of greater condensability, prove to be entirely without action toward benzene and hydrogen, a degree of specificity in catalytic action would be indicated which would hardly be anticipated on the basis of the adsorption theory of catalysis. Even before the present investigation was undertaken, however, there was indirect evidence that copper was only comparatively inactive toward benzene and hydrogen. The hydrogenation of benzene is a reaction which is reversed between 200° and 300° and, according to Sabatier,[3] copper is active in the reverse reaction above 300°. Since a catalyst for one of two opposing reactions must also be a catalyst for the other, it follows that Sabatier's copper catalyst also catalyzed the hydrogenation reaction, although the temperature at which it was active was such that the equilibrium was unfavorable to the formation of hexahydrobenzene.

It was decided to attempt the hydrogenation of benzene using as catalyst the very active copper obtained by slow reduction of the oxide in hydrogen at an initial temperature of 150°. This having been successfully accomplished, as will later be noted, an investigation by the flow method of the kinetics of the reaction in the presence of copper was undertaken in order that a comparison might be made with the somewhat similar reaction of ethylene with hydrogen.

Apparatus and Procedure.—The apparatus is shown in Fig. 1.

It consisted of a system (a) for saturating the incoming hydrogen with benzene, a catalyst bulb (c) contained in an electrically-heated furnace, a tube (d) cooled in an ice-salt mixture to remove part of the benzene and hexahydrobenzene vapors, a tube (e)

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[1] Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 368 (1905).

[2] Pease, THIS JOURNAL, **45**, 1196 (1923).

[3] Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., **1923**, par. 641.

containing silica gel to "dry" the effluent hydrogen completely, and a gas buret (f) in which the hydrogen could be collected and measured.

The general method of procedure was to pass mixtures of benzene and hydrogen of known composition over the catalyst at known rates and to determine the effluent hydrogen. The furnace and the baths surrounding the benzene saturators were brought to the desired temperatures. The flow of hydrogen was then started and the mixture passed over the catalyst for at least two hours before any readings were taken. A number of observations were then made, hydrogen being run into the gas burets for four or five minutes each time. Readings were taken over a period covering about an hour, and always until concordant results were obtained. The rate of passage was then changed as desired, half an hour allowed for the attainment of the steady state, and the observations were repeated. Knowing the composition and rate of passage of the gas mixture entering the catalyst chamber, the barometric pressure, the temperature of the gas buret and the observed volume of hydrogen, the amount of benzene converted per minute was easily calculable.

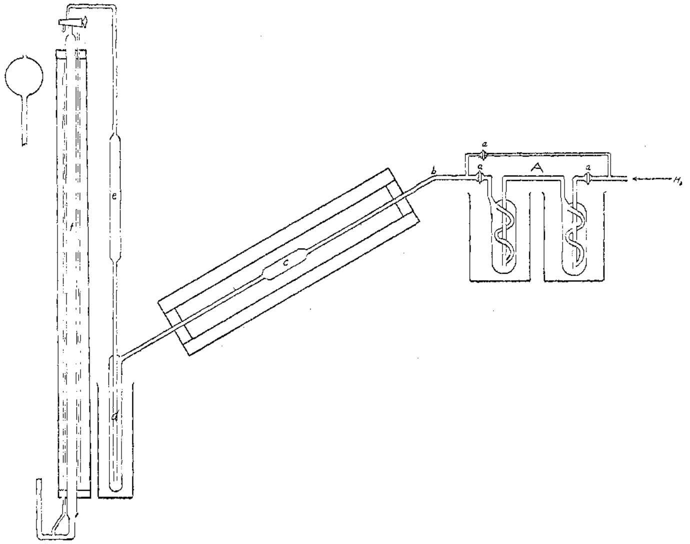

Fig. 1.—Apparatus.

Each set of runs on a particular mixture was "bracketed" by repetition of the first observations of that set, and the whole series of runs was "bracketed" at the end by repeating the observations of the first set, duplicate results showing that the activity of the catalyst had not changed appreciably during the entire course of the experiments.

In the first few runs the amount of conversion was determined by three independent methods of analysis of the reaction products: (1) the freezing point of the condensed liquid mixture was determined and its composition read from the curves of Mascarelli and Pestalozza;[4] (2) a weighed amount of the liquid mixture was shaken for ten minutes with oleum and the weight of the remaining cyclohexane determined;[5] (3) the cyclohexane and benzene were removed by means of the condenser and silica gel, the residual hydrogen was collected in the gas buret, and the conversion calculated as pointed out above. All of these methods gave results which checked within the experimental errors involved, and in the remaining runs the last method was employed, it being the most rapid and accurate.

The absence of any intermediate compounds, that is, such as C_6H_8 or C_6H_{10}, was demonstrated by adding to a portion of the condensed liquid two drops of approximately 0.004 N potassium permanganate. This was not discolored after standing for some time, indicating that neither of the unsaturated compounds mentioned above was present. The fact that the three independent methods of analysis checked one another also indicated the absence of these hydrocarbons.

The hydrogen was generated electrolytically in a cell containing 15% potassium hydroxide solution. The electrodes were coils of No. 14 nickel wire. The gas was purified by passage over hot platinized asbestos and phosphorus pentoxide. The rate of flow was calculable from the current passing through the cell and was checked by direct measurement of the volume generated per minute.

The benzene had been carefully purified and was free from thiophene. For some reason not clear to us the benzene saturators did not give a concentration corresponding to the vapor pressure at the higher temperatures. The actual concentration was determined by absorption of the benzene in a weighing tube containing silica gel and was constant for a given temperature.

The catalyst was prepared from copper oxide granules (4–16 mesh), dull black, porous granules being selected. An analysis of a sample of the oxide showed the presence of a trace of iron, but neither cobalt nor nickel was present. Hydrogen was passed through the catalyst bulb at a rate of 25 cc. per minute, and the reduction allowed to proceed at 150° until water no longer condensed in the exit tube from the furnace. This usually required from 40 to 60 hours. The temperature was then raised over a period of three hours to 200° and the reduction completed at this temperature, the total time of reduction being 80 to 100 hours. The catalyst was finally heated in a stream of hydrogen at 300° for several hours before being used in any experiments. In this way, porous granules of dull, violet-colored copper were obtained whose catalytic activity remained constant over long periods of time. Great care was taken to prevent access of air to the catalyst after preparation by keeping it always under a head of hydrogen.

The stopcocks were lubricated with a paste made by boiling together glycerol and glucose. Benzene is insoluble in this mixture.

Results and Discussion

Preliminary Measurements.—In contrast to the results of Sabatier and Senderens, we have found that active copper catalyzes the hydro-

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[4] Mascarelli and Pestalozza, *Atti. accad. Lincei,* [II] **16,** 574 (1907).

[5] Cyclohexane is only very slowly acted on by oleum whereas benzene is quite readily converted into the water-soluble benzene sulfonic acid. This effects a fairly complete separation of the two.

genation of benzene. Specifically, our most active catalyst (weighing 60 g. and having an apparent volume of 40 to 50 cc.) brought about conversion of 39% of the benzene in a mixture of 85% of hydrogen and 15% of benzene passed at the rate of 21 cc. per minute over the catalyst at 225°, and was perceptibly active at 140°. It would appear, however, that copper is distinctly less active than nickel, since Dougherty and Taylor[6] have found in their extensive investigation of the reaction in the presence of nickel that with approximately the same bulk of nickel catalyst the hydrogenation of benzene is complete at 105° when a mixture of 90% of hydrogen and 10% of benzene is passed at 30 cc. per minute.

With respect to the lesser activity of the copper, it is known that hydrogen is less strongly adsorbed by copper than by nickel and it was proposed to determine the adsorption of benzene vapor on copper and nickel.

Preliminary results on the adsorption of benzene by copper were obtained by the flow method. A given mixture of benzene and hydrogen was passed over the catalyst at 150° (where the conversion was not great) and the amount of benzene and cyclohexane coming over in unit time determined together by absorption in silica gel, observations being made until the adsorption process was complete. Hydrogen alone was then passed over the catalyst and observations were made during the desorption process. By plotting these data the total amount of benzene and hexahydrobenzene adsorbed could be determined by graphic integration. It was found that the results of the adsorption and desorption processes checked each other quite closely. These results indicated that the benzene was quite strongly adsorbed at 150°, but since all three of the components of the gas mixture were being adsorbed, the results were not particularly significant. Highly purified nitrogen, which is only very slightly adsorbed by copper, was then substituted for hydrogen in the gas mixture and adsorption measurements at 225° were begun. Unfortunately, there was appreciable conversion of the benzene into diphenyl and simultaneous de-activation of the catalyst under these conditions. This part of the investigation was, therefore, discontinued.

Reaction Rate at 140°.—Comparable results on the rate of hydrogenation of benzene in the presence of copper have been obtained at 140° by the flow method. It has been convenient to use somewhat unusual units in expressing these. For the reaction time, we have chosen to use the reciprocal of the rate of admission to the catalyst chamber of the mixture of benzene and hydrogen, expressed in minutes per cc. (N. T. P.). The benzene concentrations are expressed as volume of benzene vapor per unit quantity of hydrogen, this unit being taken as the quantity generated by one ampere in one minute. Benzene concentrations are, therefore, given in cc. (N. T. P.) per ampere-minute.

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[6] Dougherty and Taylor, *J. Phys. Chem.*, **27**, 533 (1923).

The results are presented graphically in Fig. 2. The three curves give the results of three series of measurements in which the initial compositions of the reacting mixtures were 1 molecular equivalent of hydrogen to 0.170, 0.112 and 0.085 equivalents of benzene, respectively, or 1.18, 0.78 and 0.59 cc. of benzene (N. T. P.) per ampere-minute, respectively.

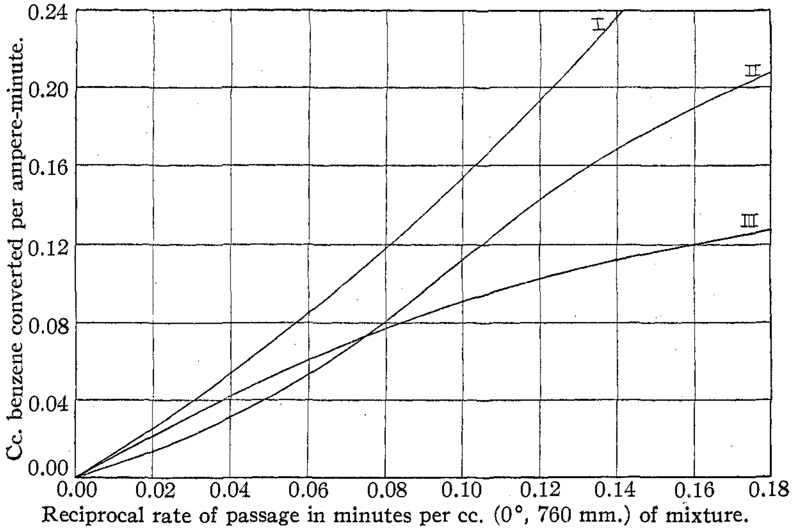

Fig. 2.—Reaction velocity at 140°. Curve I, 1 mole of hydrogen to 0.170 mole of benzene; Curve II, 1 mole of hydrogen to 0.112 mole of benzene; Curve III, 1 mole of hydrogen to 0.085 mole of benzene.

Since hydrogen was always present in considerable excess and varied in concentration only between 0.85 and 0.92 atmosphere, and since reaction was never more than about 20% complete, the kinetics of the reaction can be referred to the variation in benzene concentration alone (maximum variation 0.07 to 0.15 atmosphere). Under these conditions we might expect to find the reaction unimolecular with respect to benzene and this expectation is fulfilled at low concentrations of the latter. In Table I, are tabulated data and values of *K*, the unimolecular reaction constant,

Table I

Velocity Constant at 140°

a	x	$a-x$	t	K
0.59	0.061	0.53	0.060	1.80
.59	.078	.51	.080	1.77
.59	.092	.50	.100	1.84
.59	.103	.49	.120	1.84
.78	.169	.61	.140	1.75
.78	.191	.59	.160	1.77
.78	.209	.57	.180	1.75

calculated from the equation $K = \frac{1}{t} ln \frac{a}{a-x}$, in which t is the time of contact in minutes per cc. of gas mixture entering the catalyst chamber, a is the initial concentration of benzene in cc. (N. T. P.) per ampere-minute and x is the amount of benzene converted in cc. (N. T. P.) per ampere-minute. These data were taken from Curve III and the upper part of Curve II, Fig. 2. They are seen to satisfy the equation very well.

Data taken from Curve I and the lower part of Curve II give much lower "constants," corresponding to a relatively lower rate of reaction for the higher benzene concentrations. The curves bring this out more clearly. For short times of contact the amount of benzene converted is about the same for the three curves, whereas it should be proportional to the concentrations of benzene, which stand as 6 to 4 to 3. This can only mean that benzene acts as a poison when it is present at a concentration much greater than about 0.10 atmosphere.

These results are similar to those obtained by one of us[2] in a study of the ethylene-hydrogen combination in the presence of copper at 0° and 20°, which seems to indicate that the two actions are of the same type. In the latter study it was found that ethylene markedly hindered the reaction. Evidence was brought forward to show that ethylene was adsorbed in preference to hydrogen from a mixture of the two. The obvious conclusion to be drawn from these facts was that hydrogen must be adsorbed before reaction could take place. This has been strikingly demonstrated in some recent experiments[7] in which hydrogen was admitted to the copper catalyst before introducing the ethylene-hydrogen mixture. The initial rate of reaction was twice or thrice the normal. A similar experiment in which ethylene was first admitted proceeded at almost exactly the same rate as the normal.

We suggest that the action of benzene on the benzene-hydrogen combination at 140° is to be explained on the same grounds as the action of ethylene on the ethylene-hydrogen combination at 0°. Specifically, it is suggested that benzene is in all probability adsorbed by the copper in preference to hydrogen and that at sufficiently high concentrations of benzene this action, partially preventing as it would the adsorption of hydrogen, limits the reaction rate. Diminution of the benzene concentration would remove this hindrance to reaction but must eventually replace it with another due to the gradual disappearance of benzene as a reactant. The curves of time of contact against amount of reaction should, therefore, have a point of inflection. This is clearly present in Curve II, Fig. 2.

Temperature Coefficient and Equilibrium.—The work of Dougherty and Taylor[6] is conclusive in showing that the hydrogenation of benzene is complete in the presence of nickel from 100° up to about 200°, and accord-

[7] Experiments carried out by Mr. L. A. Stewart in this Laboratory.

ing to Sabatier[3] hexahydrobenzene is measurably dehydrogenated above 300° by nickel. The reaction is, therefore, without question incomplete in the region 200° to 300°. This conclusion is confirmed by a calculation based on the Nernst approximation formula which, in addition, indicates that the shift of equilibrium is very rapid in this region. Anomalous results for the temperature coefficient of the hydrogenation reaction are, therefore, to be expected between 200° and 300° in so far as this reaction is limited by the reverse reaction. The writers must, however, confess their inability to account fully for the results they have obtained.

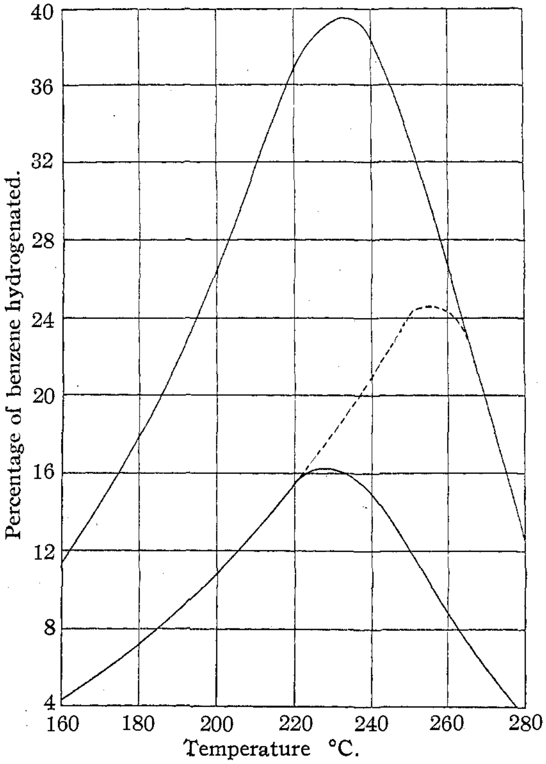

Fig. 3.—Reaction rate against temperature.

The results of our velocity-temperature measurements are shown graphically in Fig. 3. The percentage of the benzene hydrogenated has been plotted against the temperature. Measurements were made between 160° and 280° over two samples of copper catalyst using in all runs a gas mixture containing 1 molecular equivalent of hydrogen to 0.170 equivalent of benzene passed at a rate of 25 cc. per minute. Both curves rise to a maximum at 230°, beyond which temperature the percentage of conversion rapidly decreases. Judging either curve alone and having in mind the incompleteness of the reaction between 200° and 300°, one would be strongly inclined to attribute the decrease in the amount of conversion with increasing temperature above 230° to the attainment of equilibrium. It is, however, obvious that this explanation cannot hold for both curves, and the question arises whether it holds for either.

It was to be expected that the lower curve (corresponding to the less active catalyst) would meet the upper curve as indicated by the dotted line. Instead, it passes through a maximum at nearly the same temperature as does the other, although conditions must be very far removed from equilibrium at this point. Indeed the change in velocity with temperature is practically the same over the whole range for the two catalysts. The temperature coefficients as determined at 20° intervals between 160° and 280° are as follows: (upper curve values first) 1.26, 1.31; 1.22, 1.22; 1.18, 1.18; 1.02, 0.99; 0.83, 0.76; 0.69, 0.62.

We are at present engaged in a more thorough examination of this question and hope to be able to give more complete particulars as well as values for the equilibrium constant at a later date. In this connection it must be pointed out that the equilibrium data of Dougherty and Taylor[6] may very possibly be in error. After pointing out that the reaction was complete in their experiments from 100° to 200°, they continue: "......and since there are no grounds for suspecting that the temperature coefficient changes its sign after this point, it is obvious that the region 220–280° should furnish data for equilibrium calculations." This should have been a perfectly safe assumption, but the results just discussed throw some doubt on all the values except those at the highest temperature (280°) at which determinations at different rates were carried out. The anomalous results obtained by these investigators in regard to the inconstancy of the stoichiometric equilibrium constant at temperatures below 280° are doubtless to be explained on the same basis.

Summary

1. In contrast to statements occurring in the literature it has been found that metallic copper will effect the direct hydrogenation of benzene.
2. The kinetics of the hydrogenation of benzene in the presence of copper has been studied and reaction velocity measurements have been made at 140°.
3. It has been found that at sufficiently low concentrations of benzene the reaction is unimolecular with respect to benzene. At higher concentrations, benzene inhibits the reaction, the action being similar to that of ethylene in the ethylene-hydrogen combination.
4. The temperature coefficient of the reaction has been found to change in a most unusual manner in the temperature region in which reaction begins to be incomplete.

UNIVERSITY, VIRGINIA