

Kinetic Study of the Hydrogenation of Benzene over a Singly Promoted Iron Catalyst

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The hydrogenation of benzene over a singly promoted iron catalyst was studied at temperatures from 130 to 190°C, benzene partial pressures from 6.67×10^{-3} to 0.48 kPa and hydrogen partial pressures from 26.7 to 105.3 kPa, in a differential plug-flow microreactor at a total pressure just above atmospheric. Cyclohexane could be considered as the only product of the reaction, although cracking products were also found in very low concentrations at temperatures above 170°C. No cyclohexene or cyclohexadiene was detected.

The data from 130 to 180°C were correlated with an equation of the form:

$$r_0 = \frac{kK_B K_H^3 P_B P_{H_2}^3}{(1.0 + K_B P_B + (K_H P_{H_2})^4)^7}$$

suggesting that one molecule of adsorbed benzene simultaneously reacts with three molecules of dissociatively chemisorbed hydrogen as the rate-controlling step. Above 180°C, a change in the mechanism occurs.

INTRODUCTION

Considerable attention has been given in the past to the study of the hydrogenation of benzene over a variety of group VIII transition metal catalysts. In general, cyclohexane has been found to be the sole reaction product, unless elevated temperatures are employed, when cracking and rearrangement into several products occur. For the vapor phase hydrogenation, many studies have been made using nickel (1-9), platinum (10-12) and other group VIII transition metal catalysts (13). There are only a few reports on the activity of iron in the hydrogenation of benzene (14-17), and none so far on kinetic studies or mechanisms over this catalyst.

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Balandin's multiplet theory (18) predicts a planar adsorption of the benzene molecule on catalysts having an appropriate geometrical structure with lattice dimensions specifically related to the size of the benzene ring. On this basis, Trapnell (19) proposed the formation of six covalent carbon-metal bonds on the surface, followed by the simultaneous addition of all six hydrogen atoms with no formation of intermediates between benzene and cyclohexane. Since iron presents only "distorted" hexagons of metal atoms on its surface (20), it would be excluded as a catalyst for benzene hydrogenation according to Balandin. Early works (21, 22) showed the apparent inactivity of body-centered iron catalysts for the hydrogenation of benzene, but later reports (14, 16, 17) have demon-

strated the inapplicability of the geometric requirements for this reaction.

The π -complex adsorption model of the aromatic ring (23) offered a more realistic explanation for the adsorption of benzene on metal catalysts without introducing the geometric restrictions of Balandin's hypothesis. This model, however, does not solve the problem of the hydrogenation mechanism by itself (24), since hydrogenation may take place either by addition of hydrogen atoms by pairs (leading to cycloolefinic intermediates) or by random addition of single hydrogen atoms to the benzene ring with or without intermediary species. The vast but fragmented kinetic evidence from the literature appears conflicting and it does not allow the deduction of any definitive conclusion about the way that the adsorbed benzene molecule undergoes hydrogenation. Recently, Tetenyi and Barbenics (12) and Candy and Fouilloux (1) using radiotracers have found evidence of two types of chemisorbed benzene species on the surface which can be hydrogenated, one due to a single hydrocarbon-metal interaction as a π -complex and the second due to dissociative adsorption through dissociation of the carbon-hydrogen bonds of the benzene ring.

At present, the mechanism of benzene hydrogenation is far from being elucidated. Most authors acknowledge that this reaction proceeds by several sequences on the catalyst surface, but there is still no agreement on the number or on the nature of the chemical steps.

The purpose of the present work was to study the conditions under which a singly promoted iron catalyst can be active in the hydrogenation of benzene, with the view of making a kinetic study of the reaction at these conditions, and of proposing a mechanism which could explain the phenomena, since no such study has been previously reported.

METHODS

Catalyst and Reagents

Singly promoted iron 955 catalyst (7.95 wt% Al_2O_3) from the Fixed Nitrogen Laboratories of the U. S. Department of Agriculture was used for all the experiments. The catalyst was ground, and the 60 to 100 mesh fraction was used. After reduction in purified hydrogen at 500°C for 14 hr, the catalyst proved to have a surface area of 8.84 $\text{m}^2 \text{g}^{-1}$ determined by BET nitrogen adsorption.

Cyclohexane and thiophene-free benzene with a certified purity of 99 mole%, obtained from Fisher Scientific Co., were used.

Hydrogen zero gas and helium zero gas were obtained from Matheson of Canada Ltd. The hydrogen was purified by passing it through a Deoxo unit containing a palladium catalyst to remove traces of oxygen; it was further purified by passage over copper gauze and iron shavings at 320°C, a molecular sieve drier, Ascarite, and an activated charcoal trap immersed in liquid nitrogen. Helium was passed through a molecular sieve drier and an activated charcoal trap at -195.8°C, prior to its use.

Apparatus

The gas phase reaction of benzene and hydrogen was studied in a steady state plug-flow differential microreactor consisting of a 2.64 mm i.d. vertically mounted Pyrex tube. In order to avoid temperature gradients in the reactor, the catalyst was diluted in a 1:2 ratio with ground Vycor, of the same particle size as the catalyst. (Vycor showed no catalytic activity under all reaction conditions.) Typically, 30 mg of catalyst and 60 mg of ground Vycor were placed in the reactor. It was found that a total flow of 916.2 cm^3 (STP) min^{-1} across the bed was necessary in order to achieve differential conditions in the reac-

tor. The catalyst was reduced *in situ* for 14 hr at 500°C prior to its use.

The analysis of the feed and products was carried out using glc. Low levels of conversions were maintained in order to ensure differential conditions in the reactor. In most of the runs, the total conversion was below 1%.

The catalyst showed a decrease in activity of approximately 5–10% over a period of 6 hr. The bracketing method (25) was used to account for catalytic deactivation in the treatment of the kinetic data. While the hydrogen zero gas from Matheson of Canada Ltd. contained less than 20 ppm nitrogen before further purification, any nitrogen reaching the catalyst during reduction would be chemisorbed thus decreasing the initial rate per gram of catalyst (32). The slow decrease in activity at reaction temperature, however, was probably due to hydrocarbon or thermal deactivation.

RESULTS AND DISCUSSION

The gas phase reaction of benzene and hydrogen was studied over a singly promoted iron catalyst, at temperatures from 130 to 190°C , benzene partial pressures from 6.67×10^{-3} to 0.48 kPa, hydrogen partial pressures from 26.7 to 105.3 kPa, cyclohexane partial pressures from 6.67 to 46.66 Pa, in a differential plug-flow micro-reactor at a total pressure just above atmospheric. The reaction readily took place under these conditions to yield cyclohexane; no other products were detected in measurable quantities. At temperatures above 170°C , traces of low molecular weight hydrocarbons (cracking products) were detected, at concentrations several orders of magnitude below that of cyclohexane.

Experiments were also performed over unpromoted iron catalyst and cyclohexane was again the only product obtained. However, due to poor stability of the catalyst, no kinetic data were attempted. It is generally agreed that the Al_2O_3 promoter in

these fused iron catalysts serves to extend and stabilize the iron surface area (26).

The degree of conversion ranged from 0.1 to 6%, most of the data being obtained at conversion levels below 1.0%. Consequently, the partial pressures of the reactants did not vary significantly throughout the reaction zone, and the system behavior approached that of a differential reactor.

Effect of the Partial Pressure of Benzene on the Initial Rate

A series of experiments was performed at different temperatures in which the partial pressure of benzene in the feed was varied, keeping hydrogen partial pressure constant. This set of runs was done at seven different temperatures, and the results are shown in Fig. 1.

It can be observed that at a given temperature the rate of reaction increases with benzene partial pressure up to a certain value where a maximum is reached. This

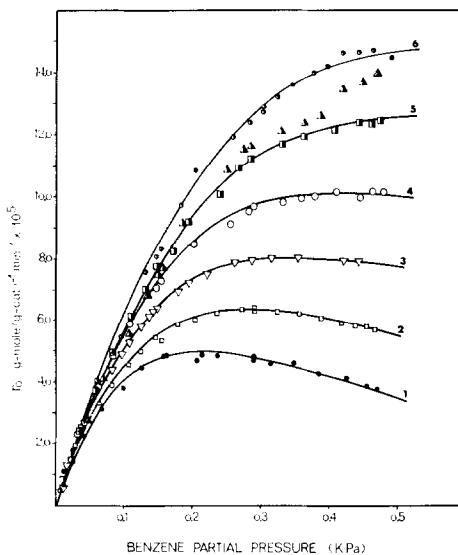


Fig. 1. Effect of the partial pressure of benzene on the initial rate of hydrogenation. For the curves indicated by 1, 2, 3, 4, 5, and 6, the temperatures were 130 , 140 , 150 , 160 , 170 , and 180°C , respectively; (Δ) points at 190°C ; (—) as predicted by Eq. (1). Hydrogen partial pressure, 105.3 kPa.

result suggests a competitive adsorption of benzene and hydrogen on the surface, with the surface reaction as the rate-controlling step.

The optimum benzene-hydrogen ratio on the surface is achieved at fairly low partial pressures of benzene, which would partially explain the apparent inactivity of iron as a catalyst for the benzene hydrogenation observed by other workers in the past (21, 22), where much higher benzene partial pressures were employed.

The partial pressure of benzene for the maximum rate increases with temperature, and, for temperatures above 170°C, the maximum occurs at benzene partial pressures over 0.48 kPa. This phenomenon can be explained by the fact (data, Figs. 6 and 7) that adsorption of benzene on the catalyst surface decreases faster with temperature than that of hydrogen and, therefore, a higher partial pressure of benzene is necessary to achieve the optimum benzene-hydrogen ratio.

The rate of hydrogenation increases with temperature. However, a maximum was observed around 180°C, as shown in Fig. 2

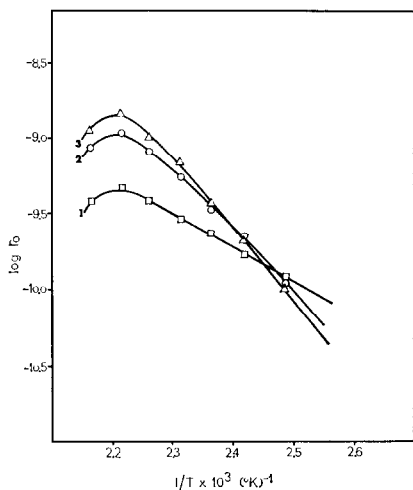


FIG. 2. Effect of temperature on the initial rate of hydrogenation. For the curves indicated by 1, 2, and 3, the benzene partial pressures were 0.15, 0.29, and 0.39 kPa, respectively. Hydrogen partial pressure, 105.3 kPa.

where the log of the initial rate is plotted as a function of $1/T$ for three different partial pressures of benzene. This phenomenon was also observed by other authors (3, 6, 9) in the same temperature range for the hydrogenation of benzene over other catalysts. So far, no conclusive explanation has been given for this observation. Amenomiya and Pleizier (27), working with an iron catalyst of the same type as that employed in the present work, found that the amount of chemisorbed hydrogen on the surface drastically decreases in the temperature range 180–200°C. Therefore, the decrease in the rate of hydrogenation above 180°C could be explained by an insufficient amount of hydrogen on the surface, hydrogen being the limiting reactant. The decrease in cyclohexane conversion rate at these temperatures can not be explained by the appearance of lower hydrocarbons since the concentration of these compounds was negligible when compared with the concentration of cyclohexane which should account for the observed decrease in the initial rate. Therefore, a change in the mechanism around 180°C is not unexpected.

Effect of the Hydrogen Partial Pressure on the Initial Rate

Experiments were performed in which the partial pressure of hydrogen in the feed was changed by dilution with helium; the benzene partial pressure and temperature were kept constant. These experiments were done at seven different temperatures. The results are presented in Fig. 3.

Figure 3 shows a strong dependence of the initial hydrogenation rate on the partial pressure of hydrogen. To better illustrate this dependency, the log of the rate was plotted against the log of hydrogen partial pressure at three temperatures as shown in Fig. 4. From the slopes of these curves it was found that the order of the reaction rate was greater than 2 with respect to the partial pressure of hydrogen, suggesting

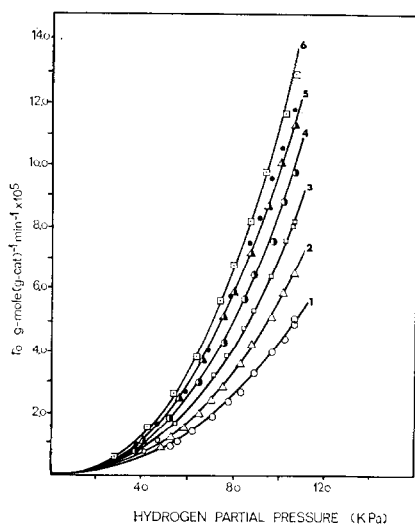


FIG. 3. Effect of the partial pressure of hydrogen on the initial rate of hydrogenation. For the curves indicated by 1, 2, 3, 4, 5, and 6, the temperatures were 130, 140, 150, 160, 170, and 180°C, respectively; (●) points at 190°C; (—) as predicted by Eq. (1). Benzene partial pressure, 0.29 kPa.

that more than two molecules of chemisorbed hydrogen are involved in the rate-controlling step for each molecule of chemisorbed benzene.

Effect of the Partial Pressure of Cyclohexane on the Initial Rate

Experiments were performed in which cyclohexane was added to the feed up to a partial pressure of 46.66 Pa, keeping the hydrogen and benzene partial pressures constant. Cyclohexane did not show inhibiting effects on the initial rate, indicating that the desorption of the product is not rate-controlling.

Reaction Mechanism

A Langmuir-Hinshelwood type reaction mechanism was found to explain the experimental observations. This mechanism postulates that one molecule of benzene chemisorbed on one active surface site simultaneously reacts with three molecules

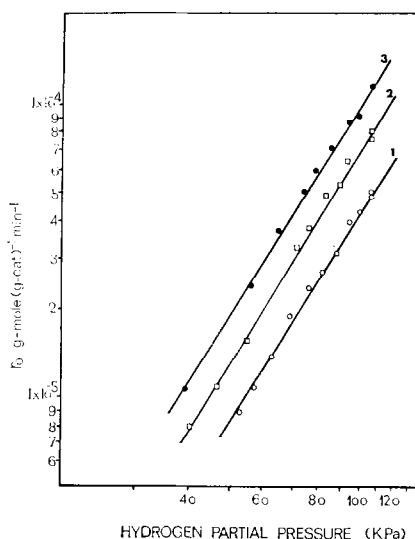


FIG. 4. Effect of the hydrogen partial pressure on the initial rate of hydrogenation on a log-log scale. For the curves indicated by 1, 2, and 3, the temperatures were 130, 150, and 170°C, respectively. Benzene partial pressure, 0.29 kPa.

of hydrogen dissociatively chemisorbed on six active surface sites, as the rate-controlling step. It is assumed that benzene and hydrogen are adsorbed on the same type of active sites at the surface.

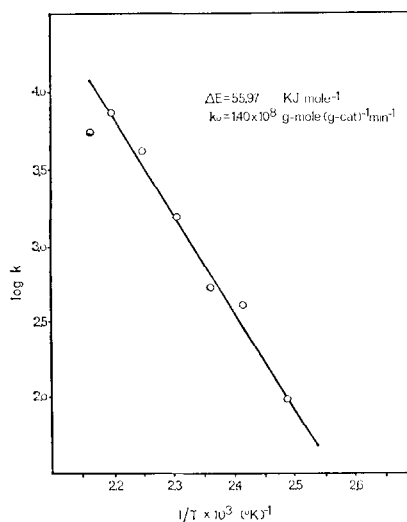


FIG. 5. Effect of temperature on the kinetic constant k of Eq. (1).

The initial rate equation for this mechanism is:

$$r_0 = \frac{kK_B K_H^3 P_B P_{H_2}^3}{[1.0 + K_B P_B + (K_H P_{H_2})^3]^7} \quad (1)$$

Equation (1) correlates the experimental data within $\pm 3\%$. The constants of the initial rate expression were determined numerically by a least-squares method for each temperature. Figures 5, 6, and 7 show the dependence of the constants of the initial rate equation on temperature, in the form of Arrhenius plots. It can be seen from these figures that the points at 190°C do not follow the general trend, indicating that a change in the reaction mechanism occurs. The activation energy, enthalpies of adsorption and preexponential factors for the constants were obtained from the slopes and intercepts of these plots in the range of 130 to 180°C .

We are aware of the limitations of postulating a reaction mechanism on the basis of kinetic studies. However, the presented mechanism and the derived rate equation give a reasonable explanation of the phenomenon and a very good interpretation of the data, whereas a simple power rate

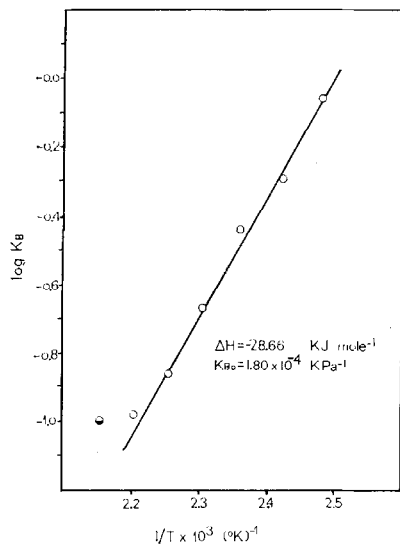


FIG. 6. Effect of temperature on the benzene adsorption constant K_B of Eq. (1).

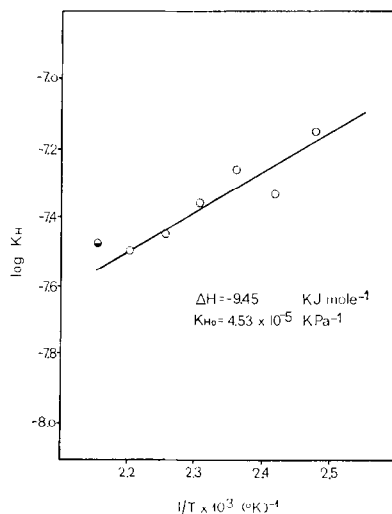


FIG. 7. Effect of temperature on the hydrogen adsorption constant K_H of Eq. (1).

equation could not reproduce the experimental information over the whole range of conditions covered.

Evidence has been obtained using several methods other than kinetics studies (1, 11, 12, 28) that the chemisorption of benzene over metals may take place by a single bond (probably of π -character). The value of the enthalpy of adsorption of benzene obtained in the present work is close to values of the enthalpies of adsorption measured independently for this compound on different surfaces under similar conditions (29). This supports the assumption of the chemisorption of the benzene ring on a single active site. On the other hand, benzene cannot be adsorbed on six iron sites due to steric considerations.

The value obtained for the activation energy of the kinetic constant is close to the values reported for the same reaction over other catalysts (4-8). In addition, the assumption made of the simultaneous reaction of three dissociated hydrogen molecules is in agreement with the observed dependence of the rate on the hydrogen partial pressure.

Evidence for the dissociative chemisorption of hydrogen on iron catalysts has been

presented (26, 27, 30, 31), indicating the possibility of the reaction of dissociated hydrogen with the benzene ring as postulated in the mechanism. The fact that the enthalpy of adsorption of hydrogen is lower than reported values for the same reaction over different catalysts (3, 7, 11), together with the observed maximum in the hydrogenation rate at temperatures around 180°C , could mean that the dissociated hydrogen H(IV) of Amenomiya and Pleizier's work (27) is the hydrogen species involved in the surface reaction. The fact that the enthalpy of adsorption of hydrogen is lower than that of benzene indicates that hydrogen is more weakly adsorbed on the surface than benzene, which is in agreement with the observation made by Basset *et al.* (11) on platinum surfaces.

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