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Gas Phase Benzene Hydrogenation on a Nickel–Silica Catalyst

I. Experimental Data and Phenomenological Description

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The hydrogenation of benzene on a nickel–silica catalyst was measured in a differential flow reactor with glc analysis of the reaction products.

The parameters varied over wide intervals. The order of reaction with respect to hydrogen rose from 0.5 at 25°C to 2–3 at 200°C. The order of reaction with respect to benzene rose from about 0.1 at 25°C to 0.3–0.5 at 200°C. No inhibition of cyclohexane could be detected. The apparent activation energies in the temperature range 25–120°C decreased from 12.5 kcal/mol at 600 Torr hydrogen pressure to 11.7 kcal/mol at 75 Torr. At higher temperatures a maximum appeared in the reaction rate. Depending on hydrogen pressure (75–600 Torr) the temperature of the maximum shifted from 135 to 180°C. Neither poisoning, nor diffusion limitation, nor approach to equilibrium could account for the maximum.

INTRODUCTION

Although much work has been done on the kinetics of benzene hydrogenation on nickel, there is still no consensus of opinion on kinetic behavior and mechanism. We should note that in most published investigations a narrow range of experimental conditions was explored. Mechanisms based on such limited data are generally not applicable to conditions outside the explored range, nor can they be considered to be unique within the range. We therefore decided to vary experimental parameters to a greater extent, hoping thus to arrive at a unique and more generally applicable mechanism. The present paper presents the experimental data we obtained in gas phase hydrogenation with hydrogen pressures between 0.1 and 1 atm and temperatures between 20 and 250°C. Measurements at higher pressures are in progress and will be published in due course.

If we take a comprehensive look at the vast but fragmented kinetic evidence from the literature, it appears at first sight conflicting, but certain trends in reported reaction orders may be noted. At temperatures below 100°C many authors (*1,3,4,6–8,10,13,15,18*) report reaction orders in hydrogen pressure between 0.5 and 0.7. At higher temperatures the order in hydrogen rises to values from 1 to 2.5 (*7,10,15,18*), ultimately reaching a value of 3 at 200°C (*21*).

In many papers (*1,3,4,6,9,13,14,20*) a near zero order in benzene pressure is reported, sometimes increasing from a low value of 0.1–0.3 at temperatures below 100°C (*7,8,10,11,15,17,18*) to about 0.5 at temperatures between 150 and 250°C (*7,10,15,18,21*). An inhibiting effect of cyclohexane is reported by some (*7,9,13*) and denied by others (*10,11,15,17,21*).

With respect to apparent activation energies there is again considerable variation but with some trends discernible. In the temperature region below 180°C on nickel films values of 7–9 kcal mol^{-1} are reported (*2,3,14*) as well as a value of 12 kcal mol^{-1} (*16*). On supported catalysts apparent activation energies ranging from 9 to 16 kcal mol^{-1} are variously reported (*1,4,6–8, 10,11,13,15,17–20*).

Near 180°C the reaction rate reaches a maximum ($E_{app} = 0$), as is mentioned for nickel by Herbo (*9*), Germain *et al.* (*7*) and Nicolai *et al.* (*15*) and for ruthenium and other metals by Kubicka (*12*). The phenomenon may also be observed in the data of Taylor (*19*). Beyond 200°C the rate falls with increasing temperature (E_{app} negative) as shown by Herbo (*9*), Nicolai *et al.* (*15*) and Zlotina and Kiperman (*21*). No firm mechanistic explanation of this maximum has been given. It has been qualitatively ascribed to poisoning (*15*) or to decrease in reactant adsorption (*7,9*).

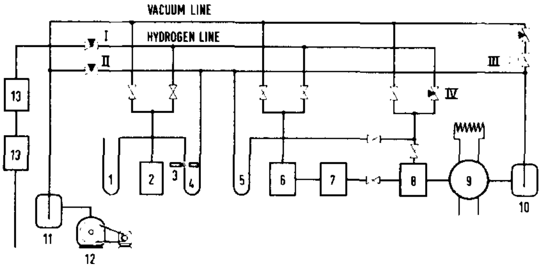

FIG. 1. Apparatus for gas phase benzene hydrogenation below atmospheric pressure. (1) Manometer, (2) reference vessel, (3) photoelectric cell, (4) manometer, (5) manometer, (6) saturator, (7) condenser, (8) reactor, (9) gas sampling valve, (10) cooltrap, (11) cooltrap, (12) rotary vacuum pump, (13) purification train.

EXPERIMENTAL METHODS

The *reactants* hydrogen and benzene were purified following the methods given elsewhere (*4*). The nickel-on-silica *catalyst* (code NZ 10) containing 11.3% Ni was reduced in the reactor for 4 hr at 450°C with 600 liters (STP) hr^{-1} (g $cat)^{-1}$ flowing through the catalyst bed. The degree of reduction was 90%, the nickel surface area was 26.2 m^2 (g $cat)^{-1}$, and the crystallite size from $D = 4310/S_{Ni}$ [see Refs. (*4,5*)] was 15.1 Å. The total BET area (N_2) was 222 m^2 (g $cat)^{-1}$, the mean pore radius 108 Å (from BET pore volume and surface area), and the particle diameter about 10 μm (from Coulter counter and microscopy).

Apparatus (*Fig. 1*). The gas phase hydrogenation was performed in a differential flow reactor. The reactor consisted of a glass tube with a porous glass disk (4, 7 or 10 mm diameter) on which the catalyst was loaded. The reactant flow pressed the catalyst particles on the porous glass disk. Different quantities of catalyst were used. At temperatures below 70°C about 100 mg catalyst was used in the reactor of 10 mm diameter (catalyst bed height, 4.5 mm). Samples of 3 to 10 mg (catalyst bed diameter, 4 mm; height, 1 to 3 mm) were used above 70°C depending on the applied hydrogen pressure. Reaction temperature was measured with an uncovered copper–constantan thermocouple (diameter of wires, 0.15 mm). The couple was not catalytically active in the benzene hydrogenation. The reduction treatment at 450°C did not affect the properties of the couple.

The reaction system of glass, consisting of a series connected benzene saturator (6), condenser (7), fixed bed differential reactor (8), gas–liquid chromatography (glc) sampling valve (9) and cold trap (10), was enclosed between two precision needle valves (I and II). The entry valve (I) was connected to a constant pressure high purity hydrogen source, the exit valve (II) to a vacuum line. Adjustment of valves (I) and (II) determined flow and pressure in the system. Constant flow and constant reactor pressure were maintained by a magnetic valve (III) bypassing needle valve (II) and controlled by a photoelectric sensor (3) on one of the arms of the mercury manometer (4). Thus the difference in pressure between the reference vessel (2) and the exit of the system was held within 1 Torr.

The flow of the incoming hydrogen was measured with a soap film flow meter. The saturator (6) and condenser (7) were thermostated, the latter at 10–20°C lower temperature than the former, ensuring the saturation pressure for benzene. At the fixed condenser temperature of 18.55°C, the benzene partial pressure was always 70.0 Torr at the exit of the condenser. The benzene pressure could be diminished by the partial bypassing of the saturator and condenser with hydrogen via needle valve (IV). The reactor equipped with a preheater spiral was also thermostated. The degree of conversion was obtained after 15 min stabilization of the flow from glc analysis of the reactor effluent (Becker research gas chromatograph type 3810, Carbowax column, catharometer detection, Kipp & Zonen integrator BC 1). Benzene partial pressure was determined from the ratio of surface areas of the peaks on the recorder of the gas chromatograph, using as standard the 70 Torr benzene peak. A correction was made for the pressure drop over the catalyst bed, as measured by manometer (5), to obtain the benzene pressure at the entrance of the reactor. Mercury contamination of the catalyst was avoided by placing the manometers downstream, except manometer (5) for a few seconds per measurement. Hydrogenation conditions: hydrogen pressure, 75–600 Torr; benzene pressure, 1–70 Torr; cyclohexane pressure, 0–50 Torr; temperature, 20–250°C. Reaction rates are expressed per unit nickel area in micromoles of H_2 per minute per square meter. Conversions were in general kept below 4%.

RESULTS

The hydrogenation of benzene to cyclohexane on the nickel–silica catalyst was measured as a function of temperature and partial pressures of hydrogen, benzene and cyclohexane. Sets of measurements were made with the rate being observed at standard conditions before and after every set. In a set the reaction temperature was decreased and/or increased, giving the same reaction rate at the same temperature and pressures. Reaction rates were reproducible within ±4%.

The effects of temperature and hydrogen pressure are shown by the Arrhenius plots in Fig. 2. The plots are linear below 110°C and yield values for E_{app}, which increase slightly with hydrogen pressure from 11.7 kcal mol^{-1} at 75 Torr to 12.5 kcal mol^{-1} at 600 Torr. Well-defined maxima in the reaction rate shift from 135°C at 75 Torr to 180°C at 600 Torr. The apparent activation energy beyond the maximum reaches a value of about -23 kcal mol^{-1}, in agreement with Zlotina and Kiperman (*21*) who found -22 kcal mol^{-1}.

From the exponential rate expression $r = k \cdot p_{H_2}^{n} \cdot p_{B}^{m} \cdot p_{cy}^{q}$, the formal reaction orders n in hydrogen, m in benzene and q in cyclohexane are derived by means of logarithmic plots; as the plots are not strictly linear, the orders are functions

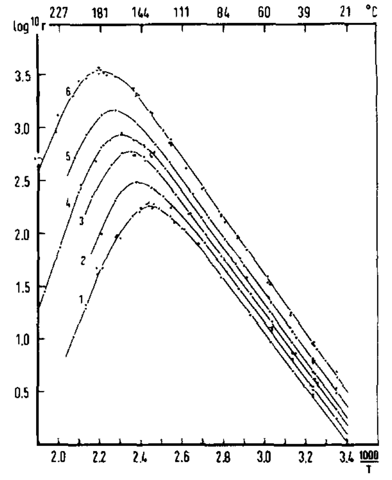

FIG. 2. Arrhenius plots showing the effect of temperature and hydrogen partial pressure on rate of benzene hydrogenation. Reaction rate r (μmol H_2 min^{-1} m^{-2}). For the curves indicated by 1, 2, 3, 4, 5, 6 the hydrogen pressures were 75, 100, 150, 200, 300, 600 Torr, respectively; benzene partial pressure, 70 Torr.

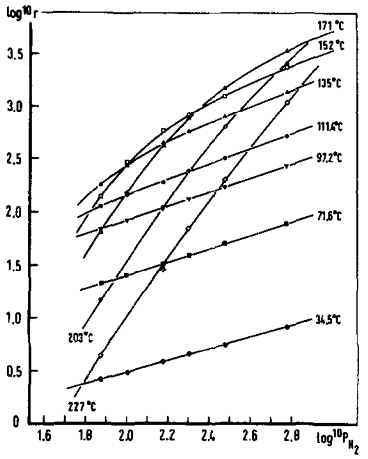

FIG. 3. Rate of benzene hydrogenation as a function of hydrogen partial pressure (from Fig. 2); pressures (Torr).

of the partial pressures involved. Figure 3 shows the effect of hydrogen pressure and temperature (data in Fig. 2) and in Fig. 4 the order in hydrogen pressure is shown. We note a smooth transition from low order (0.5–0.7) below 100°C to orders in excess of 2 at high temperature. This transition is steeper at lower hydrogen pressure. Figures 5 and 6 show the dependence of the rate on benzene pressure at various temperatures. The order in benzene pressure derived from these data is shown in Fig. 7. To gain insight into the effect of cyclohexane partial pressure on the rate, the conversion of benzene to cyclohexane was allowed to reach higher values (up to 70%) and in one experiment cyclohexane was added to the feed. A correction for the decrease in hydrogen and benzene partial pressures was made by integration over the catalyst bed. A factor can be derived to convert the experimental reaction rate at high conversion degrees (r_{uncorr}) to the reaction rate at differential

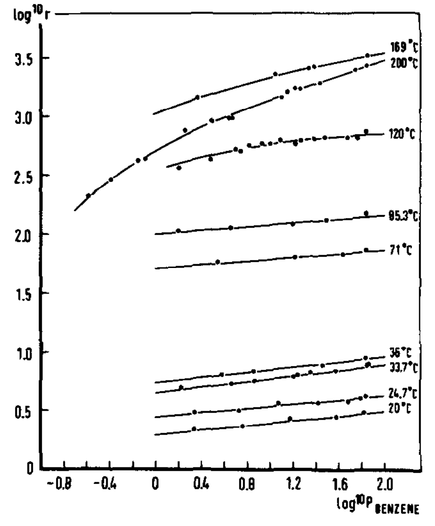

FIG. 5. Rate of benzene hydrogenation as a function of benzene partial pressure (Torr); $p_{\mathrm{H_2}} = 600$ Torr.

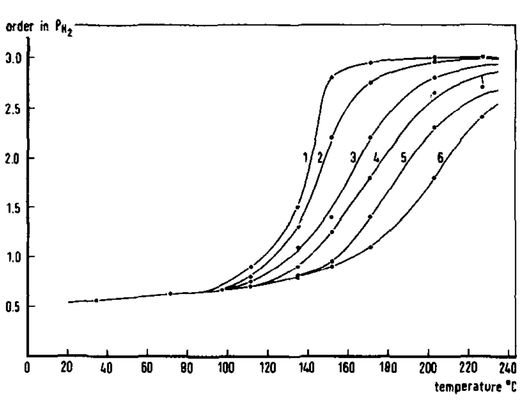

FIG. 4. Order of reaction in hydrogen pressure as a function of temperature and hydrogen partial pressure (from Fig. 3). For the curves indicated by 1, 2, 3, 4, 5, 6 the hydrogen pressures were 75, 100, 150, 200, 300, 600 Torr, respectively.

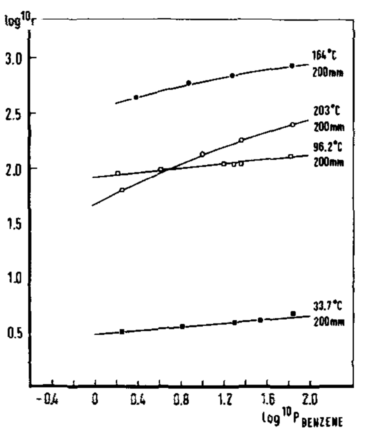

FIG. 6. Rate of benzene hydrogenation as a function of benzene partial pressure (Torr); $p_{\mathrm{H_2}} = 200$ Torr.

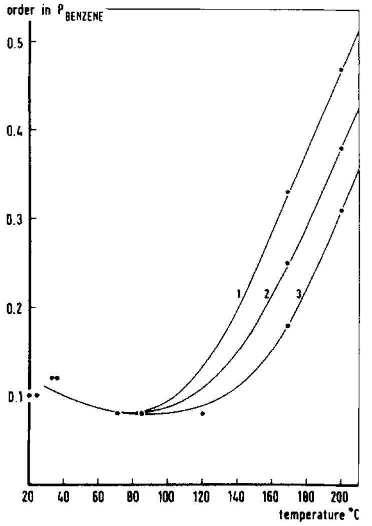

FIG. 7. Order of reaction in benzene pressure as a function of temperature and benzene partial pressure (from Fig. 5). For the curves indicated by 1, 2, 3 the benzene pressures were 2, 10, 70 Torr, respectively.

conversion (r_{corr}). With the ratio of initial pressures $p^0_{\mathrm{H_2}}/p^0_{\mathrm{B}} = a$ and with the conversion of benzene given by x, the factor is:

$$\int_0^x \frac{(1+a-3x)^{m+n}}{(1-x)^m \cdot (a-3x)^n} \cdot dx \Big/ \frac{(1+a)^{m+n}}{a^n}.$$

The integral was solved graphically for the different conditions. The influence of cyclohexane pressure on the reaction rate can be observed in Table 1, the decrease in reaction rate being nearly within the experimental error, so that we conclude that the order q in cyclohexane is zero between 25 and 200°C. Under our normal hydrogenation conditions no cracking products were found in the reaction products. When we used a catalyst sample of 500 mg at temperatures above 200°C (almost complete conversion of benzene) 1 to 2% cracking product, possibly methane, could be detected.

TABLE 1

INFLUENCE OF CYCLOHEXANE PRESSURE ON REACTION RATE OF BENZENE HYDROGENATION

r [μmol H$_2$ min^{-1} (m^2 Ni)$^{-1}$]

Temp (°C)	Torr $p_{\mathrm{H_2}}{}^0$	$p_{\mathrm{B}}{}^0$	$p_{\mathrm{cy}}{}^0$	Conv. (%)	r_{uncorr}	Corr. factor	r_{corr}
31.7	600	70	0	4.7	6.46	—	6.46
31.7	600	70	0	14.0	6.34	1.01	6.40
31.7	600	70	0	68.5	6.17	1.05	6.48
31.7	600	70	51	29	5.9	1.02	6.0
31.7	600	70	51	55	5.95	1.03	6.14
103	600	70	0	3.4	392	—	392
103	600	70	0	12.5	379	1.01	383
103	600	70	0	65	336	1.05	353
208	400	70	0	4.6	1001	—	1001
208	400	70	0	21.4	942	1.06	998
208	400	70	0	53	773	1.16	897

DISCUSSION

The general trends which we derived from fragmented and seemingly contradictory literature studies find remarkable confirmation in our experimental data, covering a wide range of conditions. Of special importance is the occurrence of well-defined maxima in the rate vs temperature plots.

The maxima in the rate of reaction versus temperature curves can be brought about by catalyst poisoning, diffusion limitation or approach to thermodynamic equilibrium. At the higher temperatures poisoning of the surface of the catalyst by organic residues is possible. However, sets of successive measurements were made with increasing and decreasing temperatures, giving the same result, showing that at the higher temperatures no irreversible catalyst deactivation occurred. Moreover, standard rates before and after each measuring series were well within experimental error (generally less than 5%). On the other hand, activities at temperatures over the maximum decrease easily by a factor of 10. Also a reversible poisoning at high temperature, disappearing with return to lower temperature, must be excluded: when we decreased very rapidly the reaction temperature, say from 220°C to the temperature of standard measurement 100°C, during a constant flow of benzene over the catalyst, no decrease in standard activity could be detected. Moreover, no cracking products could be detected in the reactor effluent. So poisoning cannot be the reason for a maximum in the reaction rate.

Also diffusion limitation might be a possible cause of rate limitation, although this can never give rise to negative activation energies. The small dimension of the catalyst particles (about 10 μm) and the large pore radius (108 Å) make the Thiele modulus small, so that even in the worst case (200°C, $p_{H_2} = 600$ Torr and $p_B = 0.7$ Torr) the effectiveness factor is very close to 1.

Approach to thermodynamic equilibrium conversion could give rise to limitations in the reaction rate. Equilibrium conversions for the equilibrium,

$$C_6H_6 + 3H_2 = C_6H_{12},$$

are shown in Table 2, together with experimental conversions at nearby temperatures. Even at the highest temperatures and lowest pressures the dehydrogenation of cyclohexane plays no part in our experiments. We therefore believe our rate data to be real over the entire range of conditions. A satisfactory mechanistic description of benzene hydrogenation should be able to describe this behavior.

In principle the appearance of a maximum is not entirely unexpected: the increase with temperature of the rate constant(s) for the surface reaction(s) will be counteracted by a decreased degree of occupation of the catalyst surface with reactants. Provided the activation energy for the surface reaction and heats of adsorption of the reactants have the right relationship a maximum can occur. This argument was already used in earlier studies (*7,9*).

TABLE 2
THERMODYNAMICS OF THE REACTION
$C_6H_6 + 3H_2 = C_6H_{12}$

Temp (°C)	$K_p{}^a$	p_{H_2}/p_B	p_{total} (Torr)	Equil. conv. (%)	Exp. conv. (%)
265	4.9	9	760	77	0.94
252	16.2	3	270	20	0.58
227	186	1	150	9.5	0.51

[a] Calculated from data given in Ref. (*22*).

In an earlier publication (*4*) we found that a very simple mechanism, involving a stepwise addition of adsorbed hydrogen atoms to adsorbed benzene, the second addition being rate determining, described our earlier data on liquid phase benzene hydrogenation below 100°C very satisfactorily. However, this mechanism is entirely unsuitable to describe the present more extensive data. Especially the occurrence of maximum rates cannot be fitted into our earlier description. We are making progress with two mechanisms proposed by Snagovskii *et al.* (*18*), both involving a stepwise addition of adsorbed hydrogen atoms to adsorbed benzene. One involves a slow step, the position of which is an adjustable parameter; the other involves a series of slow steps with equal rate constants. Both rate equations predict a maximum in the rate with temperature. The experimental data of (*18*) do not reach the temperature for maximum rate. We are now fitting the above experimental data to these mechanisms and will publish the results in due course.

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