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Gas Phase Benzene Hydrogenation on a Nickel–Silica Catalyst

IV. Rate Equations and Curve Fitting

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Three mechanisms were found suitable to describe the hydrogenation of benzene on a nickel–silica catalyst: (i) a mechanism with a rate determining step, the following hydrogen addition steps being faster; (ii) a mechanism based on the assumption that all hydrogen addition steps have the same rate constant; and (iii) a mechanism with a set of slow steps after an adjustable number of fast addition steps. With a least squares nonlinear computer fit program values of parameters for the rate equations were calculated. These values are discussed. The second mechanism appeared to be the most suitable to describe the hydrogenation of benzene.

INTRODUCTION

In preceding papers we described kinetic data (*1*), gravimetric experiments (*2*) and magnetic measurements (*3*) of the hydrogenation of benzene on a nickel–silica catalyst. In this paper we give a mechanistic description of this reaction.

In the literature many mechanisms with widely diverging basic assumptions have been proposed for the benzene hydrogenation on nickel catalysts. Several authors (*4–9*) conclude that addition of a hydrogen molecule (instead of an atom) takes place in the rate determining step, viz, the addition of the first hydrogen molecule according to (*5, 6, 8*), the second molecule according to (*7*) and the third molecule according to (*4*) and (*9*). Addition of adsorbed hydrogen atoms is assumed by Hartog *et al.* (*10, 11*), Rooney (*12*) and Snagovskii *et al.* (*13*). Snagovskii and co-workers tried two mechanisms, one with an adjustable rate determining step, the other with a set of slow steps. This last mechanism gave the best fit with his experiments. Competition on the surface of the catalyst between benzene and hydrogen is assumed by some authors (*4, 7*) and denied by others (*5, 8, 10, 11, 13*). Canjar *et al.* (*14*) used a mechanism in which benzene reacted from the gas phase. According to Jiracek *et al.* (*5*), hydrogen reacts from the gas phase. A maximum in the reaction rate at about 180°C is found by Herbo (*8*), Germain *et al.* (*7*) and Nicolai *et al.* (*15*). Nicolai *et al.* ascribed the maximum to poisoning of their catalyst, Germain *et al.* and Herbo to a decrease in reactant adsorption, but no mechanistic description was given.

The aim of this paper is to show that with different mechanisms a fairly good fit with extensive experimental data can be obtained and that a maximum in the reaction rate as a function of the temperature follows from the proposed mechanisms.

NOMENCLATURE

A	$k_+(b_{H_2}p_{H_2})^{\frac{1}{2}}/k_-$, dimensionless
b_B	Adsorption equilibrium constant for benzene, atm^{-1}

b_{H_2}	Adsorption equilibrium constant for hydrogen, atm^{-1}
F	Sum of squared differences in computer curve fitting
H	Adsorbed hydrogen atom
H	Surface coverage of adsorbed hydrogen, dimensionless
ΔH_{B}	Enthalpy of adsorption for benzene, cal mol^{-1}
ΔH_E	Enthalpy difference for equilibrium E (mech. I and III), cal mol^{-1}
ΔH_{H_2}	Enthalpy of adsorption for hydrogen, cal mol^{-1}
$\Delta H_+^{\ddagger}$	Activation enthalpy for the forward reaction, cal mol^{-1}
$\Delta H_-^{\ddagger}$	Activation enthalpy for the backward reaction, cal mol^{-1}
K_E	Constant for equilibrium E (mech. I and III), dimensionless
K_E'	$= K_E b_{\mathrm{B}} (b_{\mathrm{H}_2})^{n/2}$
k_+	Reaction rate constant of the forward reaction, molecules sec^{-1} m^{-2}
k_-	Reaction rate constant of the backward reaction, molecules sec^{-1} m^{-2}
kT/h	$= 0.208 \times 10^{11}\, T$, sec^{-1}
n	Number of hydrogen atoms added
n_s	Number of benzene adsorption sites m^{-2} Ni
p_{B}	Partial pressure of benzene, atm
p_{H_2}	Partial pressure of hydrogen, atm
r	Reaction rate, molecules sec^{-1} m^{-2}
R	Gas constant, 1.987 cal mol^{-1} $^\circ\mathrm{K}^{-1}$
ΔS_{B}^0	Entropy of adsorption for benzene, cal mol^{-1} $^\circ\mathrm{K}^{-1}$ = e.u.
ΔS_E	Entropy difference for equilibrium E (mech. I and III), e.u.
$\Delta S_{\mathrm{H}_2}^0$	Entropy of adsorption for hydrogen, e.u.
$\Delta S_+^{\ddagger}$	Activation entropy for the forward reaction, e.u.
$\Delta S_-^{\ddagger}$	Activation entropy for the backward reaction, e.u.
T	Absolute temperature, °K
X_1	Adsorption site for benzene and hydrogenated species
X_1	Free surface fraction of sites X_1, dimensionless
X_{2+n}	Adsorbed $\mathrm{C_6H_{6+n}}$
X_{2+n}	Surface coverage of $\mathrm{C_6H_{6+n}}$, dimensionless
Y	Adsorption site for hydrogen
Y	Free surface fraction of sites Y, dimensionless
α	Term allowing a shift in enthalpy of adsorption with temperature, $\Delta H' = \Delta H + \alpha T$
β	Term allowing a shift in enthalpy of adsorption with squared temperature, $\Delta H'' = \Delta H + \alpha T + \beta T^2$
θ	Surface coverage, dimensionless
σ	Standard deviation

DERIVATION OF RATE EQUATIONS

Most mechanisms proposed in the literature fail to produce an order with respect to the hydrogen pressure of 3 at high temperature decreasing to 0.5 at room temperature, nor can they account for the order with respect to the benzene pressure ranging from 0 to 1.0 (*1*).

For the derivation of rate equations the following considerations were taken into account. Since benzene and hydrogen can be considered as noncompetitive (*2*, *3*), we assign to hydrogen sites Y and to benzene, together with hydrogenated species, sites X (see Nomenclature). As the adsorption of cyclohexane in the presence of hydrogen is very small (*2*), we assume the concentration of adsorbed cyclohexane to be negligible. The dissociative character of adsorbed hydrogen was amply demonstrated by, e.g., Selwood (*16*) and Martin *et al.* (*17*). Our magnetic experiments (*3*) showed that a weakly bound form of dissociatively adsorbed hydrogen is active in the reaction. Benzene active in the reaction is assumed to adsorb associatively. Adsorbed hydrogen (*10*, *18*) and adsorbed benzene (*19*) are assumed to be in equilibrium with the gas phase.

We further started with the assumption that values for differences in entropy (ΔS) and enthalpy (ΔH) are constant over the entire range of conditions, although the heterogeneity of the surface may cause the surface coverage and temperature to have an influence on these parameters. The apparent paradox that a surface which undoubtedly has intrinsic and induced heterogeneity, behaves (pseudo)-homogeneously in kinetic studies, is discussed in some papers (*21–24*). In de Bruin's paper (*21*) a narrow band in the energy distribution appeared to play the active role in the reaction. We then have to consider for the surface reaction one kind of pseudo-homogeneously adsorbed species only and a Langmuir adsorption equation may be applied. In a narrow range of the temperature the active part of the surface may remain the same, but with a large difference in temperature as in our case (20–230°C), it might be possible that the active band shifts. A Langmuir description of the adsorption may still be applied, but with different values of the enthalpy and entropy of adsorption at different temperatures. As shown below, we had to assume such a shift in enthalpy of adsorption for benzene and also for hydrogen it might be considered.

On the basis of these considerations the hydrogenation of benzene may be considered as a sequence of hydrogen atom addition steps.

$$\mathrm{H_2(gas)} + 2\mathrm{Y} = 2\mathrm{H},$$

$$\mathrm{C_6H_6(gas)} + \mathrm{X_1} = \mathrm{X_2}, \tag{1}$$

$$\mathrm{H} + \mathrm{X_2} \rightleftharpoons \mathrm{X_3} + \mathrm{Y}, \tag{2}$$

$$\mathrm{H} + \mathrm{X_3} \rightleftharpoons \mathrm{X_4} + \mathrm{Y}, \tag{3}$$

$$\mathrm{H} + \mathrm{X_4} \rightleftharpoons \mathrm{X_5} + \mathrm{Y}, \tag{4}$$

$$\mathrm{H} + \mathrm{X_5} \rightleftharpoons \mathrm{X_6} + \mathrm{Y}, \tag{5}$$

$$\mathrm{H} + \mathrm{X_6} \rightleftharpoons \mathrm{X_7} + \mathrm{Y}, \tag{6}$$

$$\mathrm{H} + \mathrm{X_7} \rightleftharpoons \mathrm{X_8} + \mathrm{Y}, \tag{7}$$

$$\mathrm{X_8} \rightarrow \mathrm{X_1} + \mathrm{C_6H_{12}(gas)}. \tag{8}$$

Three possibilities may be distinguished: (I) hydrogen addition steps are equilibria up to a rate determining step, and further addition steps are faster. (II) All addition steps have the same rate constant. (III) As (I), except that the additions after the first slow step have the same rate constant as this step.

Mechanism I

If we assume, according to Snagovskii *et al.* (*13*), that the addition of the $(n+1)$th hydrogen atom is rate determining and that the foregoing hydrogen addition steps are in equilibrium, we may write the mechanism as:

$$\mathrm{H_2(gas)} + 2\mathrm{Y} \overset{b_{\mathrm{H_2}}}{\rightleftharpoons} 2\mathrm{H}$$

$$\mathrm{C_6H_6(gas)} + \mathrm{X_1} \overset{b_{\mathrm{B}}}{\rightleftharpoons} \mathrm{X_2}$$

$$n\mathrm{H} + \mathrm{X_2} \overset{K_E}{\rightleftharpoons} \mathrm{X}_{2+n} + n\mathrm{Y} \quad \text{equilibrium } E$$

$$\mathrm{H} + \mathrm{X}_{2+n} \xrightarrow{k_+} \mathrm{X}_{3+n} + \mathrm{Y} \quad \text{rate determining}$$

$$(5-n)\mathrm{H} + \mathrm{X}_{3+n} \xrightarrow{\text{fast}} \mathrm{C_6H_{12}(gas)} + (5-n)\mathrm{Y}$$

The surface coverages are

$$\begin{aligned} X_2 &= b_{\mathrm{B}} \cdot p_{\mathrm{B}} \cdot X_1, \\ X_{2+n} &= K_E \cdot H^n \cdot X_2 / Y^n \\ &= \exp\{\Delta S_E/R - \Delta H_E/RT\} \cdot (b_{\mathrm{H_2}} p_{\mathrm{H_2}})^{n/2} \cdot X_2 \\ &= K_E' \cdot p_{\mathrm{H_2}}{}^{n/2} \cdot p_{\mathrm{B}} \cdot X_1, \end{aligned}$$

where ΔS_E and ΔH_E are the entropy and enthalpy differences for equilibrium E. The X surface is assumed to be partly occupied by benzene and X_{2+n}, so that the following holds:

$$X_1 + X_2 + X_{2+n} = 1$$

where italic symbols represent θ-values. With these assumptions the following rate equation is derived.

$$r = k_+ \cdot H \cdot X_{2+n} = k_+ \cdot \frac{(b_{\mathrm{H_2}} p_{\mathrm{H_2}})^{\frac{1}{2}}}{1 + (b_{\mathrm{H_2}} p_{\mathrm{H_2}})^{\frac{1}{2}}} \cdot \frac{K_E' p_{\mathrm{H_2}}{}^{n/2} p_{\mathrm{B}}}{K_E' p_{\mathrm{H_2}}{}^{n/2} p_{\mathrm{B}} + b_{\mathrm{B}} p_{\mathrm{B}} + 1}.$$

Mechanism II

Assuming that the rate constants of all hydrogen addition steps to the partially hydrogenated benzene molecule are equal ($k_{+2} = k_{+3} = k_{+4} = k_{+5} = k_{+6} = k_{+7} = k_{+}$ and $k_{-2} = k_{-3} = k_{-4} = k_{-5} = k_{-6} = k_{-7} = k_{-}$) we can treat the surface coverage of all intermediates X_3 to X_7 by the steady state approximation. We saw already that X_8 is negligible.

$$X_7 = \frac{A}{A+1} X_6 = \frac{A^2}{A^2+A+1} X_5 = \frac{A^3}{A^3+A^2+A+1} X_4$$

$$= \frac{A^4}{A^4+A^3+A^2+A+1} X_3 = \frac{A^5}{A^5+A^4+A^3+A^2+A+1} X_2,$$

in which $A = (k_+/k_-)(b_{H_2}p_{H_2})^{1/2}$ and $X_2 = b_B p_B(1 - X_2 - X_3 - X_4 - X_5 - X_6 - X_7)$. By substitution we get

$$X_2 = \frac{b_B p_B(A^5 + A^4 + A^3 + A^2 + A + 1)}{b_B p_B(6A^5 + 5A^4 + 4A^3 + 3A^2 + 2A + 1) + (A^5 + A^4 + A^3 + A^2 + A + 1)},$$

$$r = k_+ H X_7 = k_+ \frac{(b_{H_2}p_{H_2})^{1/2}}{1 + (b_{H_2}p_{H_2})^{1/2}}$$

$$\times \frac{b_B p_B A^5}{b_B p_B(6A^5 + 5A^4 + 4A^3 + 3A^2 + 2A + 1) + (A^5 + A^4 + A^3 + A^2 + A + 1)}.$$

In a different way Snagovskii *et al.* (*13*) arrived at about the same expression. With the steady state treatment also expressions for the (de)hydrogenation of cyclohexene may be derived. Assuming X_2 and X_8 both zero, the degree of coverage X_3 and X_7 can be expressed in X_6 (adsorbed cyclohexene). The reaction rate of the hydrogenation of cyclohexene to cyclohexane and the dehydrogenation to benzene are, respectively:

$$r_{\mathrm{CHE \to CHA}} = k_+ H X_7 = k_+ H \frac{A}{A+1} X_6,$$

$$r_{\mathrm{CHE \to B}} = k_- X_3 = k_- \frac{1}{A^3+A^2+A+1} X_6.$$

The quotient of these reaction rates, which we measured, is

$$\frac{r_{\mathrm{CHE \to CHA}}}{r_{\mathrm{CHE \to B}}} = \frac{A^2(A^3 + A^2 + A + 1)}{(A+1)}.$$

At low temperature, when the dehydrogenation does not take place, the reaction rate of cyclohexene hydrogenation may be written:

$$r_{\mathrm{CHE \to CHA}} = k_+ H \frac{b_{\mathrm{CHE}} p_{\mathrm{CHE}} A}{b_{\mathrm{CHE}} p_{\mathrm{CHE}}(2A + 1) + (A + 1)}.$$

Mechanism III

If the hydrogen addition steps to the adsorbed benzene molecule are equilibria up to X_{2+n} and further addition steps have the same rate constant, we may consider mechanism III a combination of mechanisms I and II. In the derivation of a rate equation X_7 is expressed in X_{2+n}, similar to the expression of X_7 in X_2 for mechanism II. X_{2+n} is derived following mechanism I, with the difference that now also X_{3+n}, X_{4+n} and other intermediates must be taken into account. In this way we may derive for different values of n:

$n=0$ the same expression as for mechanism II

$n=1$ $r=k_+\mathrm{H}A^4K_E'p_{\mathrm{H}_2}{}^{\frac{1}{2}}p_\mathrm{B}/$
$[K_E'p_{\mathrm{H}_2}{}^{\frac{1}{2}}p_\mathrm{B}(5A^4+4A^3+3A^2+2A+1)+(b_\mathrm{B}p_\mathrm{B}+1)(A^4+A^3+A^2+A+1)]$,

$n=2$ $r=k_+\mathrm{H}A^3K_E'p_{\mathrm{H}_2}p_\mathrm{B}/[K_E'p_{\mathrm{H}_2}p_\mathrm{B}(4A^3+3A^2+2A+1)+(b_\mathrm{B}p_\mathrm{B}+1)(A^3+A^2+A+1)]$,

$n=3$ $r=k_+\mathrm{H}A^2K_E'p_{\mathrm{H}_2}{}^{\frac{3}{2}}p_\mathrm{B}/[K_E'p_{\mathrm{H}_2}{}^{\frac{3}{2}}p_\mathrm{B}(3A^2+2A+1)+(b_\mathrm{B}p_\mathrm{B}+1)(A^2+A+1)]$,

$n=4$ $r=k_+\mathrm{H}AK_E'p_{\mathrm{H}_2}{}^{4/2}p_\mathrm{B}/[K_E'p_{\mathrm{H}_2}{}^{4/2}p_\mathrm{B}(2A+1)+(b_\mathrm{B}p_\mathrm{B}+1)(A+1)]$,

$n=5$ the same expression as for mechanism I with $n=5$.

RATE CONSTANTS (k), EQUILIBRIUM CONSTANTS (K), ADSORPTION EQUILIBRIUM CONSTANTS (b)

All constants can be split into a temperature dependent and independent part. The surface reaction rate constants can be written according to transition state theory:

$$k_+ = n_s\frac{kT}{h}\exp(\Delta S_+{}^\ddagger/R - \Delta H_+{}^\ddagger/RT),$$

$$k_- = n_s\frac{kT}{h}\exp(\Delta S_-{}^\ddagger/R - \Delta H_-{}^\ddagger/RT),$$

in which n_s is the number of benzene adsorption sites per square meter. From (*3*) we know that at room temperature about one-fifth of the nickel metal surface is covered by chemisorbed benzene and from (*2*), that at 20°C two-thirds of the adsorbed benzene can be eliminated by hydrogenation. With a surface area of 41 Å^2 (*2*)/benzene molecule the effective n_s will be about 3×10^{17} sites m^{-2}. k_+ is expressed as the number of benzene molecules converted per second per square meter of nickel surface. To express the reaction rate in micromoles of H_2 per minute per square meter as in (*1*), a multiplication factor 3×10^{-16} is involved.

The activation entropy for the surface reaction refers to a standard state in which there is an equipartition of free surface and adsorbed species for localized species (Langmuir approach to adsorption),

$$\frac{\theta_i}{(1 - \theta_i - \theta_j - \theta_k = \cdots)} = 1,$$

and in which for mobile species (Volmer approach to adsorption),

$$\frac{\theta_j}{(1 - \theta_i - \theta_j - \theta_k - \cdots)} = 0.567,$$

holds, because then

$$\ln\frac{1 - \theta_i - \theta_j - \theta_k - \cdots}{\theta_j} = \frac{\theta_j}{1 - \theta_i - \theta_j - \theta_k - \cdots},$$

and the θ dependence of the molar differential entropy of a Volmer gas disappears (*20*).

The adsorption equilibrium constants for hydrogen and benzene may be expressed as

$$b_{\mathrm{H}_2} = \exp(\Delta S_{\mathrm{H}_2}{}^0/R - \Delta H_{\mathrm{H}_2}/RT) \quad \mathrm{atm}^{-1},$$
$$b_\mathrm{B} = \exp(\Delta S_\mathrm{B}{}^0/R - \Delta H_\mathrm{B}/RT) \quad \mathrm{atm}^{-1}.$$

The entropies of adsorption (cal g mol^{-1} °K^{-1}) refer to the standard state $p = 1$ atm, and the standard states of the adsorbed species are defined as described above.

COMPUTER CURVE FITTING

Since the number of experimental data is large, viz, 260 independent measuring

TABLE 1

Parameters for Different Mechanisms of the Benzene Hydrogenation on Nickel–Silica Catalyst NZ 10[a]

Mechanism	F	σ	$\Delta S_{+}^{\ddagger}$[b]	$\Delta H_{+}^{\ddagger}$	$\Delta S_{-}^{\ddagger}$	$\Delta H_{-}^{\ddagger}$	ΔS_E	ΔH_E	$\Delta S_{H_2}^0$	ΔH_{H_2}	ΔS_B^0	ΔH_B
I $n = 4$	1.22	6.9	−9.20	12,340			−1.09	−27,844	−31.30	−1000	−10.84	−9367
$n = 5$	1.74	8.2	−14.33	12,150			−7.00	−28,208	−23.74	−1532	−17.04	−11,470
II	0.90	5.9	−6.00	13,766	−0.08	21,149			−24.52	−2070	5.35	−1398
III $n = 1$	0.82	5.6	−10.02	13,497	3.77	22,928	1.43	−1831	−15.24	−1118	8.04	− 293
$n = 2$	1.02	6.3	−10.97	13,118	−5.68	19,206	−37.23	−23,286	−16.00	−711	44.70	16,571
$n = 3$	0.87	5.8	−15.70	12,601	14.30	28,471	−7.54	−10,473	−9.91	−415	19.08	5161
$n = 4$	1.22	6.9	−14.34	12,814	−3.17	20,373	−28.77	−26,243	−14.99	−1037	−10.00	−8277

[a] ΔS (cal mol^{-1} °K^{-1}); ΔH (cal mol^{-1}). F is the sum of squared differences; σ is the standard deviation (%).
[b] The number of active sites n_s was 3×10^{17} sites m^{-2} (see text).

points, describing 19 curves, fitting these data to a reaction rate equation with 8 or 10 parameters appears justified. We substituted the temperature dependence for the constants k, K, and b in the rate expressions and calculated the parameters for each mechanism by a nonlinear least-squares fit program. The routine finds the minimum of the sum of squared differences between experimental and calculated logarithms of reaction rates, denoted by F. A step of minimization consists of a Newton step followed by a minimization along the line defined by the Newton step. The results are given in Table 1. For different conditions the relative experimental error proved constant, so that using logarithms in curve fitting, all data receive equal weight.

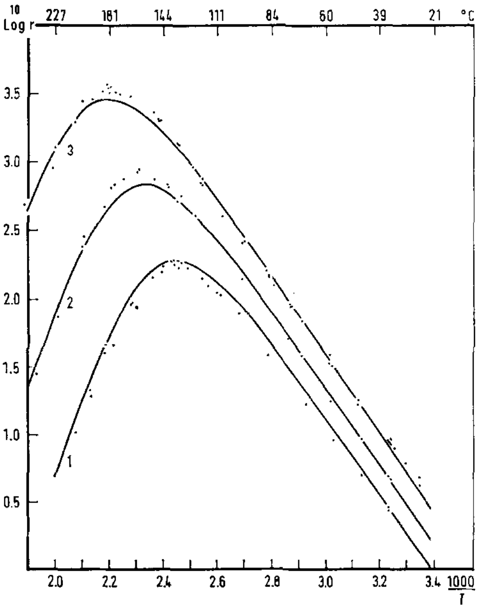

FIG. 1. Arrhenius plots showing the effect of temperature and hydrogen partial pressure on the rate of benzene hydrogenation. (●) Experimental data; (—) values for the reaction rate calculated on the basis of mechanism II. Curves 1, 2, 3: the hydrogen pressures were 75,200 and 600 Torr, respectively; benzene partial pressure, 70 Torr; catalyst NZ 10.

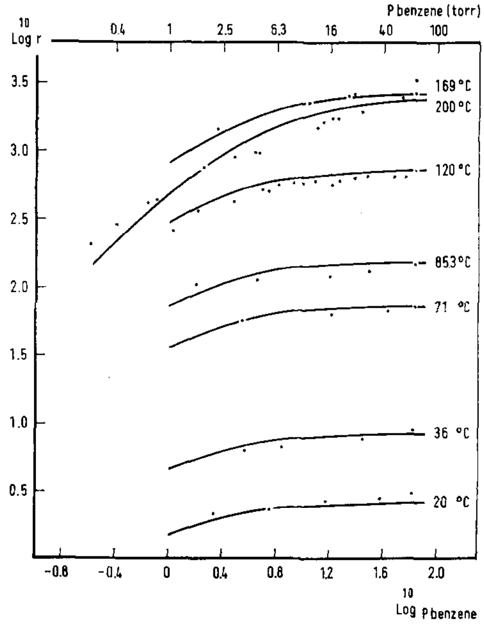

FIG. 2. Rate of benzene hydrogenation as a function of benzene partial pressure (Torr). (●) Experimental data; (—) values for the reaction rate calculated on the basis of mechanism II. Hydrogen pressure, 600 Torr; catalyst NZ 10.

The final solution arrived at was not always unique: different starting values resulted sometimes in different final values for the parameters. The apparently most reasonable values were then chosen on the basis of criteria mentioned in the discussion.

With the sets of parameters given in Table 1 it was possible to describe the hydrogenation of benzene on a nickel–silica catalyst satisfactorily. In Figs. 1 and 2 the calculated reaction rates from mechanism II are shown, next to the experimental data.

From the parameter values obtained by fitting, the surface coverage of the different surface species X_i may be computed. The results are given in Table 2.

DISCUSSION

From the σ-values in Table 1 it is evident that almost all proposed mechanisms are equally suitable to describe the hydrogenation of benzene on nickel. In Fig. 1 only the calculated values for the reaction rate from mechanism II are shown, but the other mechanisms yield about the same picture. Noteworthy is that a maximum in the reaction rate as a function of temperature, dependent on the hydrogen pressure, is obtained with all mechanisms.

In mechanism I the maximum results from the product of an increasing reaction rate constant k_+ and an above 180°C (p_{H_2} = 600 Torr) rapidly decreasing surface coverage of X_{2+n} (Table 2).

TABLE 2

Coverages of the Active Part of the Surface Accessible to Benzene, for a Number of Mechanisms, at Different Temperatures and Hydrogen Pressures[a]

Mechanism	Surface species[b]	Surface coverage				
		27°C p_{H_2} 600 Torr	135°C p_{H_2} 75 Torr	184°C p_{H_2} 600 Torr	227°C p_{H_2} 600 Torr	227°C p_{H_2} 75 Torr
I $n = 4$	X_1	0	0.011	0.033	0.157	0.166
	X_2	0	0.463	0.404	0.779	0.833
	X_6	1.000	0.562	0.563	0.064	0.001
$n = 5$	X_1	0	0.016	0.038	0.318	0.357
	X_2	0	0.411	0.207	0.580	0.642
	X_7	1.000	0.573	0.755	0.102	0.001
II	X_1	0.016	0.036	0.044	0.094	0.135
	X_2	0.164	0.275	0.273	0.512	0.728
	X_3	0.164	0.229	0.228	0.228	0.116
	X_4	0.164	0.184	0.182	0.101	0.018
	X_5	0.164	0.138	0.137	0.043	0.003
	X_6	0.164	0.092	0.091	0.017	0.0005
	X_7	0.164	0.046	0.045	0.005	0.00006
III $n = 3$	X_1	0.0013	0.183	0.045	0.069	0.114
	X_2	0.0003	0.429	0.207	0.521	0.860
	$X_3 = X_4$	0	0	0	0	0
	X_5	0.333	0.149	0.374	0.329	0.024
	X_6	0.333	0.137	0.249	0.069	0.002
	X_7	0.333	0.102	0.125	0.012	0.00014

[a] Catalyst, nickel–silica NZ 10; p_B = 70 Torr.

[b] X_1 = free surface fraction, $X_2 = (C_6H_6)_{ad}$, $X_3 = (C_6H_7)_{ad}$, $X_4 = (C_6H_8)_{ad}$, $X_5 = (C_6H_9)_{ad}$, $X_6 = (C_6H_{10})_{ad}$, $X_7 = (C_6H_{11})_{ad}$, $X_8 = (C_6H_{12})_{ad}$.

In mechanism II the quantity A appears to determine the maximum in the same way. At low temperature A is much larger than 1 and the surface coverage X_7 equals 1/6. With increasing temperature A decreases and becomes equal to 1 at the temperature where the reaction rate reaches the maximum value. This means that in the maximum the rate of the back reaction of surface intermediate X_{2+n} equals that of the forward reaction of X_{2+n} with hydrogen

$$k_+HX_{2+n} = k_-X_{2+n}.$$

Beyond the maximum A is smaller than 1 and again the surface coverage of X_7 decreases rapidly. In mechanism III the maximum in the reaction rate appears as a result of the rapid decrease of X_{2+n} *and* of X_7.

Compared to the change in X_7 the decrease in the surface coverage of hydrogen has no influence on the appearance of a maximum.

Table 2 shows that the surface coverage of benzene itself is larger at higher temperature and lower hydrogen pressure. Zlotina and Kiperman (*9*) also concluded that at 220°C benzene is much more stable on the surface than the other compounds and occupies the major part of the working surface.

The order of reaction with respect to hydrogen pressure reaches extreme values of 0.5 and 3.0 in all mechanisms except in mechanism I with $n = 4$, where an order 2.5 is the highest possible value. We therefore ruled out this mechanism. The order with respect to benzene pressure can range from 0 to 1 in all mechanisms.

Which mechanism is the best one? Solely on the basis of σ, mechanism III with $n = 1$ should be the best one. However, entropy and enthalpy differences are not just empirical parameters, their values should be physically acceptable. We will first consider the entropies and enthalpies of adsorption.

Entropies and Enthalpies of Adsorption

In all mechanisms a very small value is found for the adsorption enthalpy of hydrogen. From the values of the adsorption entropy shown and the standard entropy of gaseous hydrogen, 31 e.u., we may deduce that the hydrogen atom on the surface has still 3 to 8 e.u./g atom in the standard state. With statistical thermodynamics we calculated (*20*) that hydrogen adsorbed with two dimensional freedom, has about 5.5 e.u./g atom at 25°C and standard degree of coverage, so that $\Delta S_{\mathrm{H}_2}{}^0$ would be -20 e.u. mol^{-1}. The surface coverage for hydrogen calculated from the fit values of enthalpy and entropy of adsorption is very small, viz, about 0.01. It must be emphasized that this coverage refers to hydrogen active in the reaction, for which we found already in Ref. (*3*) that it was a small weakly bound part of the total quantity of adsorbed hydrogen.

Not all of the values found for the enthalpy and entropy of adsorption of benzene for the different mechanisms are physically acceptable. Since we considered the benzene molecule to be adsorbed associatively, a positive entropy and enthalpy of adsorption are impossible. One might, however, assume that the heat of adsorption range of the benzene converted in the reaction, shifts to higher values at higher temperatures. Accepting this, we can alter the values for the adsorption enthalpy and entropy in such a way that their changes with temperature compensate each other. If we add to the enthalpy of adsorption ΔH_{B} a term αT:

$$\Delta H_{\mathrm{B}}' = \Delta H_{\mathrm{B}} + \alpha T,$$

and add to the entropy this same α:

$$\Delta S_{\mathrm{B}}' = \Delta S_{\mathrm{B}}{}^0 + \alpha,$$

then the adsorption equilibrium constant remains unaltered:

$$\begin{aligned} b_{\mathrm{B}} &= \exp(\Delta S_{\mathrm{B}}{}^0/R - \Delta H_{\mathrm{B}}/RT) \\ &= \exp\{(\Delta S_{\mathrm{B}}{}^0 + \alpha)/R - (\Delta H_{\mathrm{B}} + \alpha T)/RT\} \\ &= \exp(\Delta S_{\mathrm{B}}'/R - \Delta H_{\mathrm{B}}'/RT). \end{aligned}$$

TABLE 3

Possible Changes in Adsorption Entropy and Enthalpy for Benzene on Nickel,[a] without Changing the Adsorption Equilibrium Constant

Mechanism	ΔS_B^{0b}	ΔH_B^b	α	$\Delta S_B'^c$	$\Delta H_B'^c$	
					300°K	500°K
I $n = 5$	−17.0	−11,470	−10	−27.0	−14,470	−16,470
			−20	−37.0	−17,470	−21,470
			−30	−47.0	−20,470	−26,470
II	5.35	−1398	−30	−24.65	−10,398	−16,398
			−40	−34.65	−13,398	−21,398
			−55	−49.65	−17,898	−28,898
III $n = 2$	44.7	16,571	−80	−35.3	− 7,429	−23,429
			−90	−45.3	−10,429	−28,429

[a] Nickel–silica catalyst NZ 10.

[b] Parameters from Table 1.

[c] $\Delta S_B' = \Delta S_B^0 + \alpha$, $\Delta H_B' = \Delta H_B + \alpha T$, ΔS in e.u., ΔH in cal mol^{-1}.

In Table 3 the values of $\Delta S_B'$ and $\Delta H_B'$ are shown for different chosen values of α.

In adsorption measurements of benzene on nickel at 0°C, Yu *et al.* (*25*) found a heat of adsorption of 25 kcal mol^{-1} at monolayer coverage. With statistical thermodynamics we estimated the entropy of benzene adsorbed on the surface at standard coverage and 25°C (*20*). For the case of mobile adsorption a value of about 31 e.u. has been found; for the case of localized adsorption about 18 e.u., yielding values for the adsorption entropy of benzene of −33 and −47 e.u., respectively. As shown in Table 3 the latter value is accompanied by rather high values of the adsorption enthalpy, so that mobile adsorption of the reactive benzene appears more probable.

Introduction in the entropy of adsorption of a term proportional to the enthalpy of adsorption, following Halsey (*27*), and a similar term as discussed above in the enthalpy, would result in an extra term proportional to T^2 in the real enthalpy of adsorption, because of the requirement that the equilibrium constants remain unchanged

$$\Delta H_B'' = \Delta H_B + \alpha T + \beta T^2$$

and

$$\Delta S_B'' = \Delta S_B^0 + \alpha + \beta T.$$

It is, however, impracticable to introduce this concept in the computations.

Since also the surface on which hydrogen adsorption occurs will be heterogeneous, it would be logical to introduce a similar temperature dependence for the adsorption enthalpy of hydrogen. However, the resulting $\Delta S_{H_2}'$ should not be lower then −20 e.u. mol^{-1}, so that only few mechanisms allow a significant value of α. In the extreme case of $\Delta S_{H_2}{}^0 = -9.9$ e.u. (mechanism III, $n = 3$) $\Delta S_{H_2}' = -20$ e.u. yields

$$\Delta H_{H_2}'(500°\text{K}) = -415 - 10 \times 500 = -5.4 \text{ kcal mol}^{-1},$$

$$\Delta H_{H_2}'(300°\text{K}) = -415 - 10 \times 300 = -3.4 \text{ kcal mol}^{-1},$$

which is still weakly adsorbed hydrogen.

Activation Entropies of Reaction, $\Delta S_+^\ddagger$ and $\Delta S_-^\ddagger$

We must now consider whether the values of $\Delta S_+^\ddagger$ and $\Delta S_-^\ddagger$ are physically acceptable.

The result of the computer fit is such that values for $\Delta S_+^\ddagger - \Delta S_-^\ddagger$ result. Separate values are then derived by introducing the value for n_s in the equation for k_+

$$k_+ = n_s \frac{kT}{h} \exp(\Delta S_+^\ddagger/R - \Delta H_+^\ddagger/RT).$$

The value of 3×10^{17} sites m^{-2} derived earlier represents the total reactive benzene capacity. We should now recall that only part of this capacity is actually reacting at any one temperature, so that the actual n_s may be much smaller. If the value of $\Delta S_+^\ddagger$ derived with $n_s = 3 \times 10^{17}$ is too small, adjustment can be made by reducing n_s, resulting in a more positive value of $\Delta S_+^\ddagger$. For mechanisms II and III $\Delta S_-^\ddagger$ must be shifted by the same amount as $\Delta S_+^\ddagger$, so that the values for $\Delta S_-^\ddagger$ in Table 1 are minimum values.

If we accept, for instance, the scheme which Rooney (*12*) proposed for the hydrogenation of benzene, the entropy of the surface complex X_{2+n} will equal approximately the entropy of the surface complex with one more hydrogen atom, X_{3+n}. The entropy difference $\Delta S_+^\ddagger - \Delta S_-^\ddagger$ of the reaction,

$$H + X_{2+n} \rightleftarrows X_{3+n}^\ddagger \rightleftarrows X_{3+n},$$

should then be mainly the loss of entropy of an adsorbed hydrogen atom, 3 to 8 e.u./g atom. The differences derived for mechanisms II and III satisfy this condition, with the exception of $n = 1$ and $n = 3$, so that we discard these mechanisms.

We now consider the separate values of $\Delta S_+^\ddagger$ and $\Delta S_-^\ddagger$. If $\Delta S_+^\ddagger$ is more negative than -8 e.u. the X_{2+n} complex loses entropy in going to the activated complex. This, in itself, does not appear impossible, since a bridge with an absorbed hydrogen atom must be formed, which reduces mobility. This difference in mobility is reflected in $\Delta S^\ddagger$, so that positive values for this quantity appear unlikely. This is an added reason to discard mechanisms III $n = 1$ and $n = 3$.

Activation Enthalpies of Reaction, $\Delta H_+^\ddagger$ and $\Delta H_-^\ddagger$

About the values of the activation enthalpies of the forward and backward reaction we can only note that their values are about the same in the different mechanisms, so that on this basis no choice can be made between mechanisms.

Entropy and Enthalpy Difference of Equilibrium E, ΔS_E and ΔH_E

If the entropy of the adsorbed species X_{2+n} is about the same as of X_{3+n}, as we assumed in the foregoing, the entropy difference of the addition of n hydrogen atoms in equilibrium E in mechanisms I and III will also be determined by the loss of entropy of adsorbed hydrogen. In mechanism III $n = 2$ the loss of the entropy of two adsorbed hydrogen atoms (-15 e.u.) in equilibrium E cannot cause the value of -37 e.u. for ΔS_E. It would imply that the adsorbed benzene molecule loses about 22 e.u. in going to X_4, so that the adsorbed X_4 species has retained 31–22 = 9 e.u. (assumption $S_{X_2} = 31$ e.u.). This value is too small even for localized adsorbed X species. Mechanism III $n = 2$ is therefore abandoned.

The enthalpy difference for equilibrium E should more or less reflect the number of hydrogen atom additions, but this trend appears only weakly from the values of ΔH_E in Table 1. The mechanisms retained so far have about the same value, so that this is not a selection criterion.

Concluding we may say that three mechanisms remain with interpretable values of the parameters: mechanism I $n = 5$, mechanism II, and mechanism III $n = 4$. On account of the smallest value of F we prefer mechanism II.

Hydrogenation and Disproportionation of Cyclohexene

Additional information may be obtained from experiments of cyclohexene disproportionation into benzene and cyclohexane. In Table 4 values are given for the ratio of the rate of hydrogenation to cyclohexane and the rate of dehydrogenation to benzene, for two different quantities of catalyst and as calculated from the parameters found for mechanism II.

According to the thermodynamics of the reaction of cyclohexene with hydrogen, only cyclohexane should be formed. If, however, by using a small quantity of catalyst, the contact time is kept small, the reaction is partly determined kinetically and benzene can desorb from the surface, as was found experimentally. With 1 mg catalyst, the experimental values for the quotient of reaction rates approach already the calculated values, and at still smaller contact times they may well become identical.

These experiments support mechanism II, because in mechanisms I $n = 5$ and III $n = 4$ the adsorbed species X_6 is in equilibrium with benzene in the gas phase. In a flow system, the benzene gas is removed and within the assumptions of mechanisms I and III, an equilibrium conversion to benzene must be established. At all temperatures this process is assumed to be rapid, and, accordingly, more benzene than cyclohexane should be formed, also at temperatures below 180°C. This was not found experimentally, so that also these experiments point to mechanism II as the best description.

An unsolved problem is that at low temperature the rate of cyclohexene hydrogenation on a nickel catalyst exceeds the rate of benzene hydrogenation by a factor 1000 [derived from Ref. (*26*)]. From mechanism II and the expression for the rate of cyclohexene hydrogenation, also derived assuming a set of slow steps, a difference in rate may be calculated of at most a factor 3 (at low temperature A was much larger than one). Possibly, the number of active sites on a nickel surface is larger for cyclohexene hydrogenation than for benzene hydrogenation, *or* directly from the gas phase, cyclohexene is adsorbed more reactively than as formed from the hydrogenation of benzene, *or* a larger part of adsorbed hydrogen is active in the cyclohexene hydrogenation, *or*, the most probable reason, it is an oversimplification to assume that the rate constants of all hydrogen addition steps in the benzene hydrogenation are equal.

TABLE 4

Cyclohexene (De)Hydrogenation[a]

Temp (°C)	$r_{\mathrm{CHE}\rightarrow\mathrm{CHA}}/r_{\mathrm{CHE}\rightarrow\mathrm{B}}$		
	65 mg cat.	1 mg cat.	Calcd[b]
160		3.65	3.63
175	20	2.11	1.35
192	4.26	1.12	0.53
201	2.45	0.79	0.34
215	1.00	0.39	0.19

[a] $p_{\mathrm{H}_2} = 315$ Torr; $p_{\mathrm{CHE}} = 67$ Torr.

[b] Calculated with the parameters found for mechanism II.

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