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Hydrogenolysis of Saturated Hydrocarbons on a Nickel Catalyst

I. Kinetics of Hydrogenolysis of Ethylcyclohexane and Reactivity of Alkylcyclohexanes

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The hydrogenolysis of a series of alkylcyclohexanes on a nickel catalyst containing 8% by weight of aluminum oxide was investigated in a flow apparatus at 220°C and under atmospheric pressure of hydrogen. In this reaction the alkyl groups were successively degraded with the formation of methane and saturated alicyclic hydrocarbons with a lesser number of carbon atoms in the side chain. The cyclohexane ring was not cleaved under the given conditions.

For ethylcyclohexane a complete kinetic analysis of the reaction was made. The experimental data satisfied a Langmuir-Hinshelwood type of relation in which the rate-determining step is a surface reaction of adsorbed molecules of the hydrocarbon and hydrogen.

The reactivities of homologous alkylcyclohexanes were compared on the basis of initial reaction rates measured under the same conditions. These data serve as a basis for considerations on the effect of the structure on reactivity and on the reaction mechanism.

INTRODUCTION

In our study of the structure effects of organic compounds on their reactivity on solid catalysts (*1*) we have given considerable attention to the hydrogenolytic cleavage of carbon bonds in different compounds. These reactions were studied in our Laboratory on a number of model compounds, such as alkylphenols (*2*), alkylbenzenes (*3*, *4*), alkylnaphthalenes (*5*, *6*), and alkylcyclanones (*7*). The hydrogenolysis of these compounds could be carried out successfully on nickel catalyst containing different amounts of aluminum oxide, under atmospheric pressure of hydrogen, and at temperatures 220–350°C; in these reactions the cleavage of carbon bonds always occurred in the alkyl groups.

Recently we have also studied the hydrogenolytic cleavage of alicyclic hydrocarbons represented by alkylcyclohexanes and some other alkylcyclanes. The present paper concerns the kinetics of hydrogenolysis of ethylcyclohexane and the study of the effect of structure on the rate of cleavage of other alkylcyclohexanes. Hydrogenolytic reactions of other hydrocarbons will be dealt with in a separate paper (*8*).

LIST OF SYMBOLS

A, B	Reactants (A, hydrocarbon; B, hydrogen)
R, S	Products of hydrogenolysis
W/F	Reciprocal space velocity of hydrocarbon (kg cat hr/mole)
f	$p_A{}^0/p_B{}^0$
k	Rate constant of surface reaction
K_A, K_B	Adsorption coefficients (atm^{-1}) of hydrocarbon and hydrogen, respectively
$p_A{}^0$, $p_B{}^0$	Initial partial pressure (atm) of hydrocarbon and hydrogen, respectively

N_A	Molar fraction of hydrocarbon
r_0	Initial reaction rate (mole/hr kg cat)
W	Weight of catalyst (kg)
x	Conversion
*	Active center on surface of catalyst
σ^*	Constant in Taft's equation which characterizes the polar (induction) effect of the substituent
ρ	Constant in Taft's equation which characterizes the type of reaction

EXPERIMENTAL

Materials used. Commercially available cyclohexane and methylcyclohexane (British Drug Houses), marked chemically pure, were used. The remaining alkylcyclohexanes needed were either prepared for this work by hydrogenation of the corresponding alkylbenzenes, taken from our laboratory supplies, or previously prepared compounds (*4*) were used. The hydrogenation of alkylbenzenes was carried out in the usual type of flow apparatus on a nickel catalyst (Ni–8% Cr_2O_3) at 140°C and under atmospheric pressure of hydrogen, with a mole ratio of hydrogen to hydrocarbon equal to 10:1. The products were freed of the residue of aromatic hydrocarbons by elution chromatography on silica, and then distilled on a laboratory column (40 TP). Their purity was tested by gas chromatography. The physical constants of the purified products (b.p. and n_D^{25}) corresponded to the values given in the literature (*9, 10*).

Electrolytic hydrogen (Bitterfeld, GDR) was taken from pressure vessels and prior to use it was purified in a column containing a commercial palladium catalyst (Chemické závody SČSP, Záluží, Czechoslovakia) and dried in a column filled with sodium hydroxide.

Bulb nitrogen (Technoplyn, Ostrava, Czechoslovakia) of at least 99.9% purity was used without further treatment.

Catalysts. Nickel catalysts containing different amounts of aluminum oxide were prepared by reducing with hydrogen a mixture of oxides obtained by coprecipitating the corresponding nitrates with an aqueous solution of potassium hydroxide. Details of the preparation have already been described elsewhere (*11*). For kinetic measurements we took the size fraction of mixed oxides from 0.5 to 1.0 mm, which was reduced for 4 hr with hydrogen at 350°C directly in the flow apparatus immediately before the experiment. The compositions of the different reduced nickel catalysts, and their total surface areas determined by the BET method, are given in Table 1.

TABLE 1

COMPOSITION OF NICKEL CATALYSTS AND THEIR TOTAL SURFACE AREAS AFTER REDUCTION WITH HYDROGEN

Al_2O_3 (% by weight)	Surface area (m^2/g)
0.0	8.3
2.0	38.0
8.0	85.0
15.0	99.0
28.0	161.0
48.2	245.0
65.3	300.0
100	333.0

Apparatus and experimental procedure. The kinetic measurements of alkylcyclohexane hydrogenolysis were carried out in a standard glass flow apparatus with a fixed bed of catalyst (*12*) at 220°C. The amount of catalyst used in the kinetic measurements was in the range 0.125–3.0 g. For each measurement we used a fresh portion of catalyst, which was reduced directly in the apparatus. The temperature of the reaction was measured with an accuracy of ±0.5°C in the bed of catalyst by a thermocouple sheathed by a glass tube running down the center of the reactor.

The products of hydrogenolysis were condensed at −78°C and analyzed chromatographically. The conversion of alkylcyclohexane was calculated from the composition of the liquid products of hydrogenolysis only, and it was found that this procedure gave sufficiently reliable results.

Because it was found that the activity of the catalyst decreases somewhat in the initial phase of each experiment, it was necessary to attain steady state conditions at which the temperature and rate of flow of the reactants through the bed of catalyst were constant and, the activity of the catalyst no longer varied. Only when such conditions had been attained were three samples taken over a period of 15–20 min; the mean value of the conversion determined from the analysis of the three samples was taken as representative for one kinetic measurement.

Analytical methods. The liquid products of hydrogenolysis were analyzed by gas-liquid chromatography in an instrument with heat-conductivity detection. The stationary phase consisted of Apiezon L and dioctyl sebacate, respectively, coated on porous earthenware, and amounting to 7% of the support weight. Separate 100-cm columns were prepared with two stationary phases. With the combination of the two stationary phases we succeeded in separating both the homologous alkylcyclohexanes and the corresponding alkylbenzenes. The temperature of the column was set according to the molecular weight of the substances contained in the mixtures to be analyzed (90–140°C). Nitrogen was used as the carrier gas. The content of the individual components in the analyzed sample was determined from the areas under the corresponding peaks on the chromatogram, on the basis of calibration with mixtures prepared from the pure components.

RESULTS AND DISCUSSION

Composition of the Nickel Catalyst and Its Activity

As can be seen from Fig. 1, the highest activity for the hydrogenolysis of ethylcyclohexane at 220°C is displayed by the catalyst containing 8–10% by weight of aluminum oxide and 92–90% by weight of nickel. Catalysts of these compositions have already been found active in the hydrogenolysis of alkylphenols (*2*) and alkylcyclohexanones (*7*). The structure and catalytic properties of this type of nickel catalyst have been studied earlier by Jošt and Bažant (*11*) but they have not succeeded in finding the cause of the highest hydrogenolytic activity of the above-mentioned catalyst. It is possible to ascribe the high reactivity of ethylcyclohexane on the nickel catalyst containing 10% aluminum oxide by weight to the suitable adsorptivity of the investigated compounds.

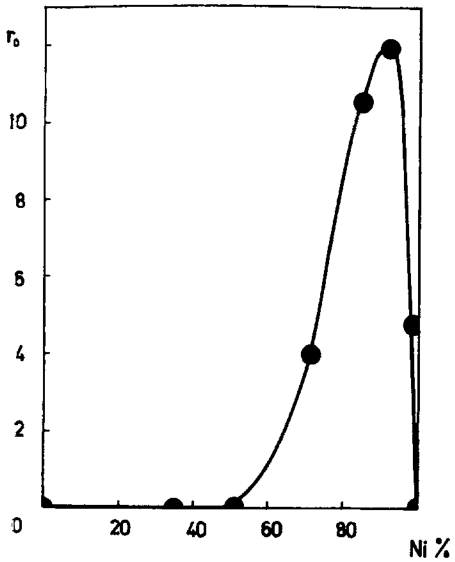

FIG. 1. Dependence of the activity (expressed as r_0) on the composition of nickel catalysts for hydrogenolysis of ethylcyclohexane at 220°C and under partial pressure of hydrogen 0.87 atm; mole ratio of hydrogen:ethylcyclohexane = 6.9:1; total pressure 1 atm.

Therefore, the adsorption coefficients of some alicyclic and aliphatic hydrocarbons on nickel catalysts containing different amount of Al_2O_3 are at present being measured in our Laboratory by the pulse flow method.

Product Composition of Hydrogenolysis of Alkylcyclohexanes

The hydrogenolytic cleavage of carbon bonds in the side chains of alkylcyclohexanes can be conceived as a certain kind of hydrogenolysis of alkanes in which one end of the paraffin chain is blocked by the cyclohexyl group. Only methylcyclohexane is a somewhat exceptional case because the carbon atom of the cyclohexane ring is part of the reaction center. However, the temperature range of hydrogenolysis of alkyl-

TABLE 2

PRODUCTS OF HYDROGENOLYTIC SPLITTING OF ALKYLCYCLOHEXANES ON Ni–8% BY WEIGHT Al_2O_3 CATALYST AT 220°C AND PARTIAL PRESSURE OF HYDROGEN 0.87 ATM

	Composition of reacted fraction (mole %)				
Hydrocarbon	Cyclohexane	Methylcyclohexane	Ethylcyclohexane	Propylcyclohexane	Isopropylcyclohexane
Methylcyclohexane	100	—	—	—	—
Ethylcyclohexane	—	100[a]	—	—	—
Propylcyclohexane	—	100[b]	—	—	—
Butycyclohexane	—	32	12	56[c]	—
	—	23	18	59[d]	—
Isopropylcyclohexane	—	13	87[e]	—	—
	—	—	100[f]	—	—
sec-Butylcyclohexane	—	—	—	100[g]	—
Isobutylcyclohexane	—	—	—	100[h]	—
tert-Butylcyclohexane	—	—	40	—	60[i]

For conversion up to

[a] $x = 0.25$.

[b] $x = 0.03$.

[c] $x = 0.04$.

[d] $x = 0.03$.

[e] $x = 0.20$.

[f] $x = 0.10$.

[g] $x = 0.18$.

[h] $x = 0.10$.

[i] $x = 0.10$.

cyclohexanes in considerably limited as compared with those of the alkanes, because under atmospheric pressure of hydrogen and at temperatures above 230°C dehydrogenation of the cyclohexane ring already takes place. Under the chosen reaction conditions the cyclohexane ring was quite stable against hydrogenolytic splitting and its dehydrogenation took place only to a very small extent (a maximum of 3% conversion to the corresponding aromatic hydrocarbon).

As is apparent from Table 2, hydrogenolytic cleavage of carbon bonds in alkyl groups appears to be a predominantly successive reaction. That we did not succeed in identifying the primary products of successive degradation of the side chain of propylcyclohexane is probably partly due to the fact that ethylcyclohexane is substantially more reactive than the original hydrocarbon (see Table 5), and also is probably due to direct spliting of the ethyl group from the alkyl chain. With hydrocarbons with branched side chains, successive degradation of the individual branches of the chain was also observed. In Fig. 2 we give as an illustration the course of hydrogenolysis of *tert*-butylcyclohexane. The results of experiments with isopropylcyclohexane and *tert*-butyl and *sec*-butylcyclohexane reveal that the simultaneous splitting off of two or more terminal methyl groups occurs in none of the listed cases.

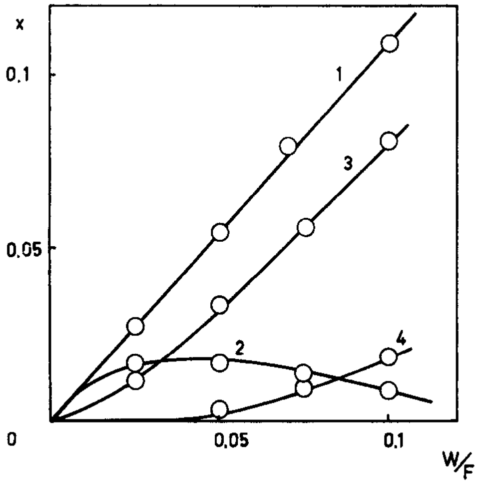

FIG. 2. Course of hydrogenolysis of *tert*-butylcyclohexane on nickel catalyst (8% Al_2O_3) at 220°C and partial pressure of hydrogen 0.87 atm, mole ratio of hydrogen:*tert*-butylcyclohexane = 6.9:1; total pressure 1 atm. 1, Total conversion; 2, conversion to isopropylcyclohexane; 3, to ethylcyclohexane; 4, to methylcyclohexane.

The successive degradation of alkyl groups has already been observed with aromatic hydrocarbons (*3–6*) and alkylcyclanones (*7*).

Kinetic Analysis

As in our previous work (*5, 7, 13*), we also apply in the present case of hydrogenolysis of alkylcyclohexanes the kinetic approach of Langmuir and Hinshelwood. For the model substance we used ethylcyclohexane, which under the given conditions reacts according to the simple scheme (A). The reactivity of the methylcyclohexane formed is very low, and under the reaction conditions used it does not undergo further change. For the bimolecular reaction of ethylcyclohexane hydrogenolysis a large number of kinetic equations can be proposed. Equations for the initial rates of bimolecular heterogeneous catalytic reactions have been dealt with comprehensively in the work of Penčev and Beránek (*3*), who recently studied the hydrogenolysis of isopropylbenzene.

$$C_6H_{11}{-}CH_2{-}CH_3 + H_2 \rightarrow C_6H_{11}{-}CH_3 + CH_4 \quad (A)$$

In the kinetic analysis we first verified the assumptions that inner and outer diffusion have no effect on the reaction rate. Experiments with catalysts of different granular size (0.125–0.30; 0.30–0.50; 0.50–1.0 mm) always gave the same conversion of ethylcyclohexane. Also changes in the mass flow rate of reactants at constant space velocity (*F/W*) did not affect the composition of the reaction products.

The purpose of a further series of measurements was to determine the dependence of the initial rates of hydrogenolysis of ethylcyclohexane on the partial pressures of the reactants. The values of the initial reaction rates were read from plots of the dependence of the conversion of ethylcyclohexane (x) on the reciprocal space velocity (*W/F*) at a constant mole ratio of the reactants and at constant temperature. As can be seen from Fig. 3, for conversions from 0.1 to 0.15 the plot of these dependences is a straight line starting from the origin. In Fig. 4 is shown the dependence of the initial rate of ethylcyclohexane hydrogenolysis on its mole fraction. As is apparent, up to the mole fraction of ethyl-

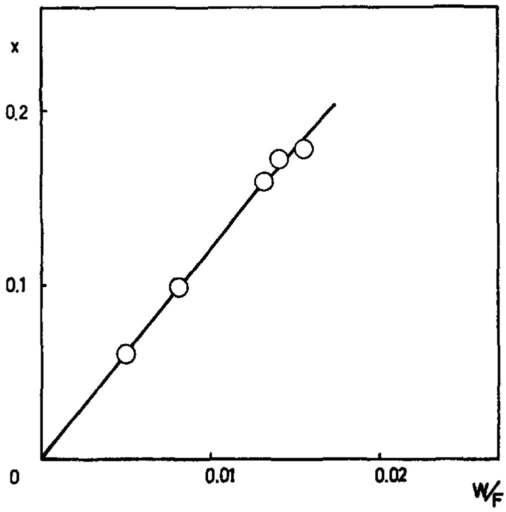

FIG. 3. Dependence of ethylcyclohexane conversion (x) on nickel catalyst (8% Al_2O_3) on the reciprocal space velocity (*W/F*), at 220°C and partial pressure of hydrogen 0.82 atm; mole ratio of hydrogen:ethylcyclohexane = 6.9:1; total pressure, 1 atm.

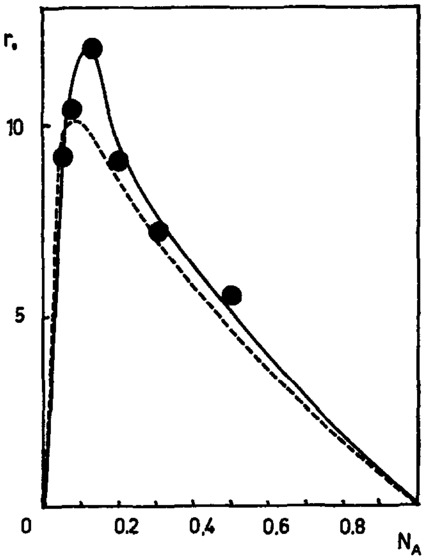

FIG. 4. Dependence of initial reaction rate (r_0) of ethylcyclohexane hydrogenolysis on the mole fraction of the hydrocarbon (N_A), at 220°C and total pressure 1 atm; - - - - -, theoretical course corresponding to mechanism expressed by Eq. (14) resp. (17).

cyclohexane 0.14 hydrogen increases the rate of hydrogenolysis: above the quoted value the reaction rate decreases, which indicates that hydrogen begins to retard the rate of hydrogenolysis.

Further, we investigated the dependence of the effect of partial pressure of ethylcyclohexane on the initial rate, at constant mole ratios of hydrocarbon and hydrogen. The partial pressure of ethylcyclohexane was reduced by diluting the reaction mixture with nitrogen. The results obtained for three mole ratios of the reacting components are shown in Fig. 5.

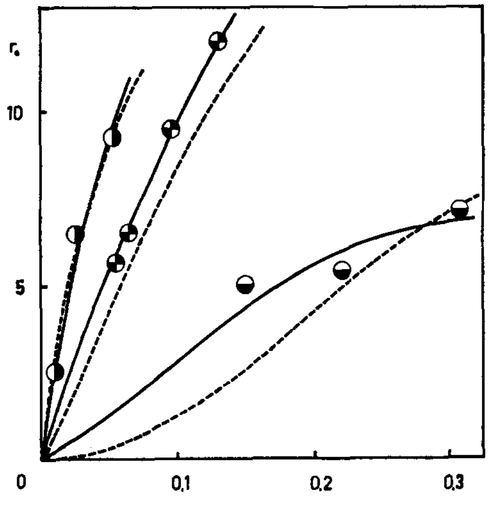

FIG. 5. Dependence of initial reaction rate (r_0) of ethylcyclohexane hydrogenolysis on partial pressure of the hydrocarbon (p_A^0), at 220°C; total pressure 1 atm; curve 1 (mole ratios of hydrogen: hydrocarbon) 18.6:1; 2, 6.91:1; 3, 2.34:1; -----, theoretical course corresponding to mechanism expressed by Eq. (14), resp. (17).

The forms of the plots shown in Figs. 4 and 5 allowed immediate exclusion from further consideration kinetic mechanisms in which the rate-determining step is the desorption of the product or the adsorption of any one of the reaction components. In order to be able to decide between kinetic equations in which the rate-determining step is a surface reaction (see Table 3) we treated the experimental results mathematically. As can be seen from Table 3, we took into consideration those cases in which the hydrocarbon is absorbed [Eqs. (1)–(6)] and hydrogen reacts from the gaseous phase, and in which both components are adsorbed [Eqs. (7)–(14)]. We did not taake into consideration those cases in which hydrogen is adsorbed and the hydrocarbon reacts from the gaseous phase, because these are also excluded by the form of the dependences shown in Figs. 3 and 4.

From the experimental data we first calculated the variables appearing in the linearized forms of the rate equations, which were then treated by the method of double linear regression, using the computer NE 803. For example, the linearized form of the rate equation (7) was statistically treated in the form

$$y = a_0 + a_1x_1 + a_2x_2,$$

where x_1 and x_2 were the independent variables, and y the dependent variable,

$$y = [(p_A{}^0)^2 f/r_0]^{1/2}, \qquad x_1 = p_A{}^0, \qquad x_2 = p_A{}^0f$$

By this procedure the values of the coefficients (a_0, a_1, a_2) were obtained and the rate constant and adsorption equilibrium constants were calculated subsequently

$$a_0 = (1/kK_AK_B)^{1/2}, \quad a_1 = (K_A/kK_B)^{1/2}, \quad a_2 = (K_B/kK_A)^{1/2}$$

$$k = 1/a_1a_2, \qquad K_A = a_1/a_0, \qquad K_B = a_2/a_0$$

These calculated values were used as first estimates in the grid search method (*13, 14, 15*), by which more accurate values were obtained. For the criterion of suitability we took the sum of squares of the differences between the calculated and experimentally determined initial reaction rates for all experiments

$$S = r_0{}^2{}_{(\text{calc})} - r_0{}^2{}_{(\text{exptl})}$$

The values which provide criteria for the proposed kinetic mechanisms are given in Table 4. The most probable mechanisms seem to be those expressed by Eqs. (7), (12), (13), (14). These kinetic models corresponds to the assumption that the rate-determining step is the surface reaction of

TABLE 3

KINETIC EQUATIONS FOR INITIAL REACTION RATES OF THE REACTION A + B = R + S WHEN A SURFACE REACTION IS THE RATE-DETERMINING STEP

Number of equation	Kinetic equation	Linearized form[a]
(1)	$r_0 = kK_Ap_A{}^0p_B{}^0/(1 + K_Ap_A{}^0)^2$	$[(p_A{}^0)^2f/r_0]^{1/2} = (1/kK_A)^{1/2} + (K_A/k)^{1/2}p_A{}^0$
(2)	$r_0 = kK_Ap_A{}^0p_B{}^0/(1 + K_Ap_A{}^0)^3$	$[(p_A{}^0)^2f/r_0]^{1/3} = (1/kK_A)^{1/3} + (K_A{}^2/k)^{1/3}p_A{}^0$
(3)	$r_0 = kK_Ap_A{}^0p_B{}^0/(1 + K_Ap_A{}^0)^4$	$[(p_A{}^0)^2f/r_0]^{1/4} = (1/kK_A)^{1/4} + (K_A{}^3/k)^{1/4}p_A{}^0$
(4)	$r_0 = kK_Ap_A{}^0p_B{}^0/[1 + (K_Ap_A{}^0)^{1/2}]^2$	$[(p_A{}^0)^2f/r_0]^{1/2} = (1/kK_A)^{1/2} + (1/k)^{1/2}(p_A{}^0)^{1/2}$
(5)	$r_0 = kK_Ap_A{}^0p_B{}^0/[1 + (K_Ap_A{}^0)^{1/2}]^3$	$[(p_A{}^0)^2f/r_0]^{1/3} = (1/kK_A)^{1/3} + (K_A{}^{1/6}/k^{1/3})(p_A{}^0)^{1/2}$
(6)	$r_0 = kK_Ap_A{}^0p_B{}^0/[1 + (K_Ap_A{}^0)^{1/2}]^4$	$[(p_A{}^0)^2f/r_0]^{1/4} = (1/kK_A)^{1/4} + (K_A/k)^{1/4}(p_A{}^0)^{1/2}$
(7)	$r_0 = kK_AK_Bp_A{}^0p_B{}^0/(1 + K_Ap_A{}^0 + K_Bp_B{}^0)^2$	$[(p_A{}^0)^2f/r_0]^{1/2} = (1/kK_AK_B)^{1/2} + (K_A/kK_B)^{1/2}(p_A{}^0) + (K_B/KK_A)^{1/2}(p_A{}^0f)$
(8)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{(1 + K_Ap_A{}^0 + K_Bp_B{}^0)^3}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/3} = \left(\dfrac{1}{kK_AK_B}\right)^{1/3} + \left(\dfrac{K_A{}^2}{kK_B}\right)^{1/3}(p_A{}^0) + \left(\dfrac{K_B{}^2}{kK_A}\right)^{1/3}(p_A{}^0f)$
(9)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{(1 + K_Ap_A{}^0 + K_Bp_B{}^0)^4}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/4} = \left(\dfrac{1}{kK_AK_B}\right)^{1/4} + \left(\dfrac{K_A{}^3}{kK_B}\right)^{1/4}(p_A{}^0) + \left(\dfrac{K_B{}^3}{kK_A}\right)^{1/4}(p_A{}^0f)$
(10)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + K_Ap_A{}^0 + (K_Bp_B{}^0)^{1/2}]^3}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/3} = \left(\dfrac{1}{kK_AK_B}\right)^{1/3} + \left(\dfrac{K_A{}^2}{kK_B}\right)^{1/3}(p_A{}^0) + \left(\dfrac{K_B{}^{1/2}}{kK_A}\right)^{1/3}(p_A{}^0f)^{1/2}$
(11)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + K_Ap_A{}^0 + (K_Bp_B{}^0)^{1/2}]^4}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/4} = \left(\dfrac{1}{kK_AK_B}\right)^{1/4} + \left(\dfrac{K_A{}^3}{kK_B}\right)^{1/4}(p_A{}^0) + \left(\dfrac{K_B}{kK_A}\right)^{1/4}(p_A{}^0f)^{1/2}$
(12)	$\mathrm{r}_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + (K_Ap_A{}^0)^{1/2} + K_Bp_B{}^0]^3}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/3} = \left(\dfrac{1}{kK_AK_B}\right)^{1/3} + \left(\dfrac{K_A}{k^2K_B{}^2}\right)^{1/6}(p_A{}^0)^{1/2} + \left(\dfrac{K_B{}^2}{kK_A}\right)^{1/3}(p_A{}^0f)$
(13)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + (K_Ap_A{}^0)^{1/2} + K_Bp_B{}^0]^4}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/4} = \left(\dfrac{1}{kK_AK_B}\right)^{1/4} + \left(\dfrac{K_A}{kK_B}\right)^{1/4}(p_A{}^0f)^{1/2} + \left(\dfrac{K_B{}^3}{kK_A}\right)^{1/4}(p_A{}^0f)$
(14)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + (K_Ap_A{}^0)^{1/2} + (K_Bp_B{}^0)^{1/2}]^4}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/4} = \left(\dfrac{1}{kK_AK_B}\right)^{1/4} + \left(\dfrac{K_A}{kK_B}\right)^{1/4}(p_A{}^0)^{1/2} + \left(\dfrac{K_B}{kK_A}\right)^{1/4}(p_A{}^0f)$
(15)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + 2(K_Ap_A{}^0)^{1/2} + K_Bp_B{}^0]^3}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/3} = \left(\dfrac{1}{kK_AK_B}\right)^{1/3} + \left(\dfrac{64K_A}{k^2K_B{}^2}\right)^{1/6}(p_A{}^0)^{1/2} + \left(\dfrac{K_B{}^2}{kK_A}\right)^{1/3}(p_A{}^0f)$
(16)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + 2(K_Ap_A{}^0)^{1/2} + K_Bp_B{}^0]^4}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/4} = \left(\dfrac{1}{kK_AK_B}\right)^{1/4} + \left(\dfrac{16K_A}{kK_B}\right)^{1/4}(p_A{}^0f)^{1/2} + \left(\dfrac{K_B{}^3}{kK_A}\right)^{1/4}(p_A{}^0f)$
(17)	$r_0 = \dfrac{kK_AK_Bp_A{}^0p_B{}^0}{[1 + 2(K_Ap_A{}^0)^{1/2} + (K_Bp_B{}^0)^{1/2}]^4}$	$\left[\dfrac{(p_A{}^0)^2f}{r_0}\right]^{1/4} = \left(\dfrac{1}{kK_AK_B}\right)^{1/4} + \left(\dfrac{16K_A}{kK_B}\right)^{1/4}(p_A{}^0f)^{1/2} + \left(\dfrac{K_B}{kK_A}\right)^{1/4}(p_A{}^0f)^{1/2}$

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[a] In the linearized forms the partial pressure of hydrogen is expressed by the relation $p_B{}^0 = p_A{}^0f$.

TABLE 4

MATHEMATICAL TREATMENT OF RESULTS OF THE KINETIC STUDY OF ETHYLCYCLOHEXANE HYDROGENOLYSIS ON Ni—8% Al_2O_3 CATALYST

Number of equation	Linear regression			Grid search method			
	k	K_A	K_B	k	K_A	K_B	S
1	58.96	8.72	—	53.02	9.43	—	26.00
2	111.10	4.08	—	91.82	4.32	—	30.69
3	163.90	2.64	—	129.54	2.78	—	33.80
4[a]	—	—	—	—	—	—	—
5	95.20	78.00	—	85.68	51.48	—	20.46
6	232.50	14.29	—	203.67	10.59	—	21.15
7	76.34	15.41	1.43	84.54	18.76	1.20	8.76
8	316.57	5.37	0.66	366.01	6.21	0.45	14.67
9	1283.00	3.15	0.44	1163.00	3.25	0.17	21.16
10	217.39	8.00	2.22	339.00	8.25	0.89	14.28
11	941.30	4.01	0.74	1470.50	4.26	0.28	18.38
12	138.60	164.87	1.09	152.00	133.13	0.94	8.31
13	800.74	19.28	0.45	847.62	18.98	0.41	7.75
14	793.95	25.66	0.63	880.75	31.26	0.60	7.44
15	554.40	41.21	1.09	608.00	33.28	0.94	8.31
16	3202.96	4.82	0.45	3390.48	4.75	0.41	7.75
17	3175.80	6.42	0.63	3523.00	7.82	0.60	7.44

[a] Negative values of the coefficients (a_0, a_1) of the kinetic equation (4) were found and therefore this mechanism has no physical meaning.

adsorbed ethylcyclohexane with adsorbed hydrogen. Unfortunately it was not possible to decide unambigously whether the adsorption of one or both reactants took place without or with dissociation, although for the later case the criterion acquires the lowest values.

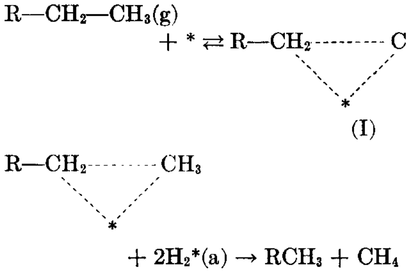
The kinetic equations (12), (13), and (14) in which the symmetrical dissociative adsorption of the hydrocarbon is assumed must be modified to the forms (15), (16), (17), corresponding to asymmetrical dissociation which is only possible in the case of ethylcyclohexane [for details see ref. (*3*)].

The criteria of suitability for Eqs. (15), (16), (17) have the same values as those for Eqs. (12), (13), (14), because the factor 2 at the adsorption term of the hydrocarbon in the denominator acts as a constant and only influences the values of the rate constants and the adsorption coefficient of ethylcyclohexane.

On the basis of the kinetic results some conclusions about the chemical mechanism of hydrogenolysis can be drawn.

If the Eq. (7) is valid then it can be assumed that the hydrogenolysis proceeds in the stages (B)–(D).

$$H_2(g) + * \rightleftarrows H_2^*(a) \qquad (B)$$



$$R{-}CH_2{-}CH_3(g) + * \rightleftarrows \underset{*}{R{-}CH_2\cdots CH_3}(a) \qquad (C)$$

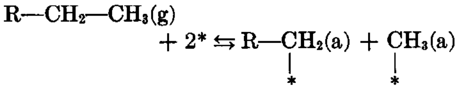
(I)

$$\underset{*}{R{-}CH_2\cdots CH_3} + 2H_2^*(a) \rightarrow RCH_3 + CH_4 + 2^* \qquad (D)$$

Equations (B) and (D) represent the equilibrium adsorption of hydrogen and ethylcyclohexane on the surface of the nickel catalyst. Equation (D) describes the rate-determining step in which the C–C bond is completely cleaved, and methylcyclohexane and methane are formed. The molecular adsorption of ethylcyclohexane is probably connected only with partial dissociation of C–C bonds, as is schematically shown in the structure of the surface species (1).

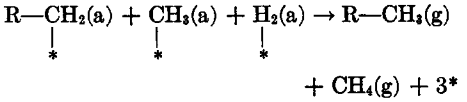
If kinetic equations (12), (13), (14),

resp. (15), (16), (17), are valid, then the adsorption of ethylcyclohexane proceeds with dissociation

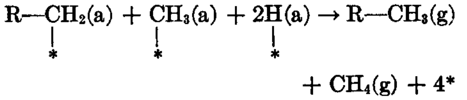


$$\mathrm{R{-}CH_2{-}CH_3(g)} + 2^* \leftrightarrows \underset{*}{\underset{|}{\mathrm{R{-}CH_2(a)}}} + \underset{*}{\underset{|}{\mathrm{CH_3(a)}}} \qquad \text{(E)}$$

The rate-determining step involves the reaction of surface-bonded radicals with hydrogen [Eqs. (F) or (G)] according to the kinetic equations (13), (14), resp. (16), (17)



$$\underset{*}{\underset{|}{\mathrm{R{-}CH_2(a)}}} + \underset{*}{\underset{|}{\mathrm{CH_3(a)}}} + \underset{*}{\underset{|}{\mathrm{H_2(a)}}} \rightarrow \mathrm{R{-}CH_3(g)} + \mathrm{CH_4(g)} + 3^* \qquad \text{(F)}$$



$$\underset{*}{\underset{|}{\mathrm{R{-}CH_2(a)}}} + \underset{*}{\underset{|}{\mathrm{CH_3(a)}}} + \underset{*}{\underset{|}{\mathrm{2H(a)}}} \rightarrow \mathrm{R{-}CH_3(g)} + \mathrm{CH_4(g)} + 4^* \qquad \text{(G)}$$

Although Eqs. (C) and (E) were derived from two different kinetic mechanisms their chemical meaning is very similar and expresses only the different degree of dislocation of electrons in the C–C bond during the adsorption of the hydrocarbon molecule.

The formation of the surface-bonded radicals assumed in Eqs. (E)–(G) is in good agreement with the conception put forward by different authors (*17–21*) on the mechanism of hydrogenolysis on metal catalysts.

Effect of the Structure of Alkylcyclohexanes on Their Reactivity

The reactivities of the different alkylcyclohexanes were compared on the basis of the values of the initial reaction rates of hydrogenolysis, which were measured under constant partial pressure of the hydrocarbon and at a constant mole ratio of the two reactants. The results obtained are summarized in Table 5. It can be seen that the reaction rate of hydrogenolysis decreases from ethylcyclohexane to *n*-butylcyclohexane, and similarly from isopropylcyclohexane to isobutylcyclohexane. This phenomenon is probably due to the increasing displacement of the cyclohexyl group from the reaction center and is associated with the electronic action of this group. In the study of hydrogenolysis of alkyl aromatic hydrocarbons (*4, 6*) the induction effect of the substituent on the reaction rate was also proved and correlations by Taft's equation were obtained. In the case of alkylcyclohexanes an analogous procedure is not possible, however, because values of the constant σ^* have not yet been published for alkylcyclohexyl groups.

However, since it is known (*22*) that the relative decrease in the value of σ^* for alkylcyclohexyl groups must be proportional to its changes for other substituents, we used for correlating the rate data of hydrogenolysis of alkylcyclohexanes the values σ^* for alkylphenyl groups (Table 5).

TABLE 5

INITIAL REACTION RATES OF THE HYDROGENOLYSIS OF ALKYLCYCLOHEXANES AND POLAR CONSTANTS σ^* CHARACTERIZING DIFFERENT SUBSTITUENTS

Hydrocarbon	Substituent R′[a]	r_0[b] (mole/hr/kg$_{\mathrm{cat}}$)	r_0^{rel}	σ^*[c]
Methylcyclohexane	C_6H_{11}	0.1	0.1	0.600
Ethylcyclohexane	$C_6H_{11}CH_2$	12.0	17.1	0.215
Propylcyclohexane	$C_6H_{11}CH_2CH_2$	1.6	2.3	0.080
Butylcyclohexane	$C_6H_{11}CH_2CH_2CH_2$	0.7	1.0	0.020
Isopropylcyclohexane	$C_6H_{11}(CH_3)$	13.0	18.6	0.110
Isobutylcyclohexane	$C_6H_{11}CH_2CH(CH_3)$	1.7	2.4	0.060
sec-Butylcyclohexane	$C_6H_{11}CH(CH_2CH_3)$	4.0	5.7	0.040
tert-Butylcyclohexane	$C_6H_{11}C(CH_3)_2$	2.4	3.4	0.020

[a] Substituent R′ includes the carbon atom of the reaction center and also the bonded group (R′ = R–CH$_2$).

[b] For 220°C, Ni–8% Al_2O_3, $p_B{}^0$ 0.87; mole ratio of hydrogen to hydrocarbon, 6.9:1.

[c] Instead of the polar constant σ^* for C_6H_{11} the value for C_6H_5 was used; values taken from ref. (*4*).

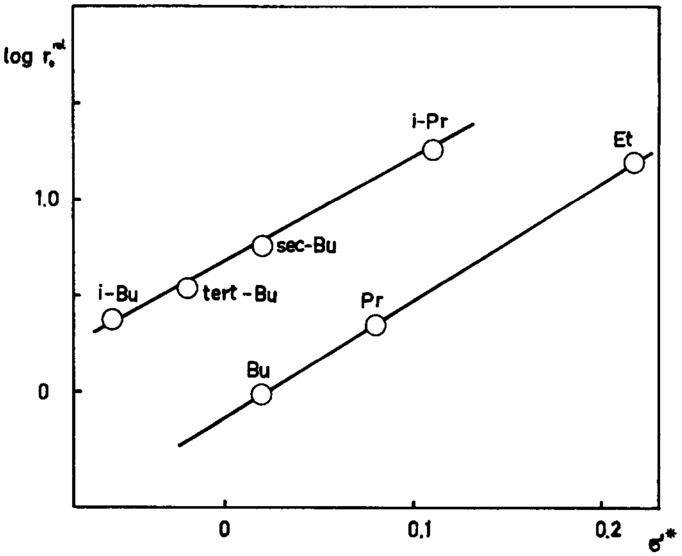


FIG. 6. Linear correlation of reactivities of alkylcyclohexanes in their hydrogenolysis on a nickel catalyst (8% Al_2O_3) at 220°C; Taft's equation.

The correlation according to Taft's equation (H) is shown in Fig. 6.

$$\log r_0^{rel} = \text{const} + \sigma^*\rho \qquad \text{(H)}$$

Although this procedure does not enable us to determine the correct value of the constant ρ it does show that the electronic effects in the hydrogenolysis of alkylcyclohexanes are the same as those in the hydrogenolysis of alkylbenzenes. Comparing the relative reaction rates of hydrogenolysis of alkylcyclohexanes (Table 5) with the corresponding alkylbenzenes (*4*) and alkylnaphthalenes (*6*), it seems clear enough that the structure has a more pronounced effect on reactivity in the series of alicyclic than in aromatic hydrocarbons.

It is interesting to note, however, that for the hydrogenolysis of both alkylbenzenes and alkylcyclohexanes the correlation according to Taft's equation gives two distinct linear relationships. The data for compounds from which during hydrogenolysis a methyl group is split off from a secondary carbon atom in the alkyl chain fall on one straight line, whereas those for hydrocarbons from which a methyl group is split off from a tertiary or quaternary carbon atom fall on the other straight line. The different behavior of the two groups of alkylbenzenes in hydrogenolysis was explained (*4*) by the action of steric effects which impede methyl groups from splitting off from a carbon atom on which the chain is branched.

In the series of alkylcyclohexanes it was found, however, that hydrocarbons with branched chains are more reactive than the isomeric *n*-alkylcyclohexanes. This means that the difference in the reactivities of these two groups of hydrocarbons is probably due to other effects. The correlation of reactivities was carried out for both the series of alkylbenzenes and alkylcyclohexanes on the basis of the initial reaction rates of hydrogenolysis, which are a function of the rate constants and of the adsorption coefficients of the reactants. It cannot be excluded therefore that the difference in adsorptivities of the two types of hydrocarbons on nickel catalysts containing different amounts of aluminum oxide (8% for alkylcyclohexanes, 50% alkylbenzenes) could be one of the reasons for the observed difference in reactivities of hydrocarbons with a straight and branched side chain.

Of the investigated compounds, the reactivity of methylcyclohexane was found to be the lowest, and similarly to toluene (*4*), it did not fit Taft's equation. The anomalous behavior of this hydrocarbon can be explained by the fact that the reaction center is on a carbon atom which is part of the cyclohexane ring.

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