

INVESTIGATION OF HYDROGENATION IN LIQUID PHASE. XXVI.*
 KINETICS OF PARALLEL-CONSECUTIVE REACTIONS
 IN HYDROGENATION OF 4-VINYLCYCLOHEXENE

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The kinetics of a complex reaction system at hydrogenation of 4-vinylcyclohexene on a palladium catalyst in a hexane medium is studied. Measurements were performed in a mixed batch reactor at a temperature of 20°C and at atmospheric pressure. The rate and adsorption constants of all reaction components were estimated and the system was described by Langmuir-Hinshelwood equations. The respective system of kinetic equations was integrated numerically and the calculated concentration dependences of reaction components on time were found to be in a good agreement with the experimental values. In hydrogenation on larger catalyst particles, a change in selectivity for the given reaction system was determined.

The hydrogenation kinetics of 4-vinylcyclohexene on a palladium catalyst in liquid phase is studied. Such more complex reaction systems with hydrogenation in liquid phase have been so far seldom studied¹⁻⁵. This paper represents a continuation of kinetic studies^{4,5} in which the reaction systems have been studied on model reactions that simulate some reactions applicable in industrial practice. Hydrogenation of 4-vinylcyclohexene was studied in papers⁶⁻⁹ where the aim was to follow the succession of hydrogenation of individual bonds in a molecule of 4-vinylcyclohexene⁶⁻⁸ and an effort was made to prepare a selective catalyst for the production of vinylcyclohexane⁷ or of a mixture of ethylcyclohexenes⁹.

THEORETICAL

Under the assumption that the reaction system at hydrogenation of 4-vinylcyclohexene can be described by the Langmuir-Hinshelwood kinetic relations it is possible to obtain the time dependences of concentrations of individual reaction components by solution of the following differential equations (individual quantities are denoted like those in the Scheme 1):

$$-(V/W) (dC_A/dt) = (k_1 + k_2) K_A C_A / R, \quad (1)$$

$$(V/W) (dC_B/dt) = [k_1 K_A C_A - (k_3 + k_4) K_B C_B] / R, \quad (2)$$

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$$(V/W)(dC_C/dt) = (k_4 B_B C_B + k_6 K_D C_D - k_5 K_C C_C)/R, \quad (3)$$

$$(V/W)(dC_D/dt) = [k_1 K_A C_A - (k_6 + k_7) K_D C_D]/R, \quad (4)$$

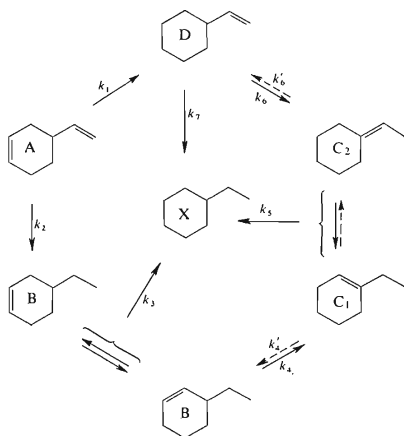
$$C_X = C_A^0 - C_A - C_B - C_C - C_D, \quad (5)$$

$$(R = 1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D). \quad (6)$$

Initial conditions:

$$t = 0; \quad C_A = C_A^0; \quad C_B = C_C = C_D = C_X = 0. \quad (7)$$

It has been assumed in derivation of Eqs (1) to (7) that the reaction components with a double bond are adsorbed far more than paraffines, *i.e.* the final product (ethylcyclohexane) and solvent (hexane). Thus in denominator of the equations are not included the terms corresponding to the final product ($K_X C_X$) and the solvent. As long as the reaction takes place in the kinetic region the hydrogen concentration in the liquid phase is constant (it equals to the equilibrium solubility of hydrogen in the reaction mixture at a respective temperature and pressure) and is implicitly included, together with the adsorption constant of hydrogen in the constants k_i and K_i . An analogous system of differential equations has also been used for description of concentration dependences on time for hydrogenation of reaction intermediates *i.e.* of 4-ethylcyclohexene and vinylcyclohexane.



SCHEME 1

Equations (1) to (7) have been solved by the numerical method of Runge-Kutte¹⁹ (computer Hewlett-Packard 2116 B) with the rate and adsorption constants estimated from experimental data.

EXPERIMENTAL

Chemicals used. The 4-vinylcyclohexene was prepared by the Diels-Alder synthesis from butadiene (Kaučuk, Kralupy n. Vlt.)⁷. The pure product was obtained from the raw mixture by rectification in a column with five theoretical plates at reflux ratio 1 : 10. The boiling point of the product was 128°C and n_D^{20} 1.4637 and it was chromatographically pure. The 4-ethylcyclohexene was prepared by partial hydrogenation of 4-vinylcyclohexene on a Raney nickel W2 catalyst¹⁰. Reaction was carried out in a batch reactor at 50°C and hydrogen pressure 30–150 at. Raw product contained approx. 80% of 4-ethylcyclohexene and 20% ethylcyclohexane. The mixture was separated in a preparation gas chromatograph Beckman (USA), (for conditions see¹¹). The b.p. of the obtained product was 132°C and n_D^{20} 1.4470 with the chromatographic purity higher than 99%. The 3-ethylcyclohexene was prepared by Grignard synthesis from ethylmagnesium bromide and 3-bromocyclohexene¹². The distilled 3-ethylcyclohexene had the b.p. 129.5°C and n_D^{20} 1.4447. 1-Ethylcyclohexene¹³ was prepared by dehydration of 1-ethylcyclohexanol by the *p*-toluenesulphonic acid with 1-ethylcyclohexanol produced by the Grignard reaction of ethylmagnesium bromide with cyclohexanone. The prepared product was a mixture of 94% of 1-ethylcyclohexene and 6% of ethylidencyclohexene with the b.p. 137°C which could not be separated by distillation¹³. Vinylcyclohexene was prepared by pyrolysis of 2-cyclohexylethanol acetate. The 2-cyclohexylethanol was produced by catalytic hydrogenation of 2-phenylethanol on the Raney-Nickel W2 catalyst at a temperature of 150°C and hydrogen pressure¹¹ 135 at. The temperature of pyrolysis was 500°C. The layers of the reaction mixture containing acetic acid, vinylcyclohexene and ethylidencyclohexene were separated and the hydrocarbon layer was heated for 2 hours with sodium using a reflux condenser. By distillation was obtained vinylcyclohexene (b.p. 127°C and n_D^{20} 1.4498). Another part was obtained in an analogous way by pyrolysis of the palmitate of 2-cyclohexylethanol at 350°C (see¹³). Ethylcyclohexene¹¹ was prepared by hydrogenation of 4-vinylcyclohexene on the 3% weight Pd/active carbon at 60°C and hydrogen pressure 30–150 at. The rectified product had the b.p. 136°C and n_D^{20} 1.4332. The 2-methyl-1-propanol (anal. grade purity, Lachema, Brno) was used. Hexane (anal. grade purity, Schuchardt, GFR) was prior to use rectified in the column with 15 theoretical plates. Hydrogen (technical quality B, Technoplyn, Pardubice) was rectified before use on the nickel kieselguhr catalyst¹⁴ and copper on kieselguhr¹⁵ at 150°C.

The catalyst used contained 3% weight Pd on active carbon. An industrially produced catalyst No 9041 (new product 41–00) was used (CHZ ČSSP, Záluží v Krušných horách). The catalyst carrier is formed by active carbon with narrow pores Bensorbon HB-3 (Hrušovské Chemické závody). For kinetic measurements the size of the used particles was less than 0.04 mm and for the study of the effect of thermal diffusion the size of particles was in the range 1.2 to 1.5 mm.

Apparatus. Hydrogenation of 4-vinylcyclohexene was made in an isothermal ideally mixed glass batch reactor¹⁶ that was designed for the study of parallel consecutive reactions⁵. In the used reactor it was easy to reach the kinetic region as regards the mass transfer outside the catalyst particle¹⁷. The internal diffusion effect was in the experiments eliminated by the use of a sufficiently small catalyst particles (0.04 mm) for which at hydrogenation of cyclohexene was measured fraction of active internal surface higher than 90% on the same catalyst. The rates of cyclohexene^{18,19} and 4-vinylcyclohexene hydrogenation are approximately comparable.

Measurement procedure. Into the reactor kept at constant temperature was introduced a weighed amount of catalyst (0.02 to 1.0 g according to the hydrogenation rate) and 100 ml hexane as the solvent. The apparatus was washed by hydrogen and at slow mixing the catalyst was activated for 30 min. The reaction started after addition of the hydrogenated substrate into the reactor (0.2 to 3.0 g) and after increasing the mixing rate to 1.000 r.p.m. In time intervals (2–15 min according to the reaction rate) were by use of a syringe taken samples of the reaction mixture from the reactor (maximum 0.2 ml) which were analyzed chromatographically.

Analytical method. The chromatographic analysis of the reaction mixture was made with the Chrom-2 apparatus (Laboratorní přístroje, Prague) with the flame-ionization detector. The operating conditions: Glass column 3.5 m long, inside diameter 2.5 mm, filled with Chromatone N—AW (particles 0.2 to 0.25 mm) containing 15% of polyethylene glycol (6000), 68°C, the carrier gas N₂, flow rate 1.5 ml/min, flow rate of hydrogen 50 ml/min; feeding of the sample of 1 to 5 ml directly by the syringe into the column. Under these conditions were determined the relative retention times of reaction components (values are related to the inside standard of 2-methyl-1-propanol): Hexane — 0.13; ethylcyclohexane — 0.36; vinylcyclohexane — 0.43; 4-ethylcyclohexene — 0.54; 3-ethylcyclohexene — 0.54; 1-ethylcyclohexene — 0.59; ethylidencyclohexane — 0.59; 4-vinylcyclohexene — 0.63. It was not possible to determine analytically 4-ethylcyclohexene in the presence of 3-ethylcyclohexene and 1-ethylcyclohexene in the presence of ethylidencyclohexane. This fact did not affect the kinetic measurements due to a low equilibrium content²¹ of 3-ethylcyclohexene and ethylidencyclohexane in the reaction mixture. Further, for evaluation of the reaction pattern has been assumed that olefins with the bond substituted in the same manner are hydrogenated with the same rate²¹.

RESULTS AND DISCUSSION

In accordance with the measured results the reaction pattern of hydrogenation of 4-vinylcyclohexene (Scheme 1) has been proposed. As it was impossible to determine

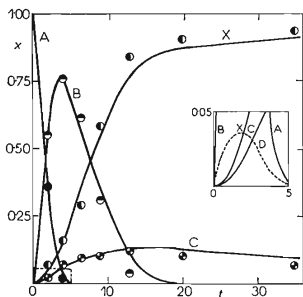


FIG. 1

Concentration Dependence of Reaction Components on Time at Hydrogenation of 4-Vinylcyclohexene on Pd/C at 20°C

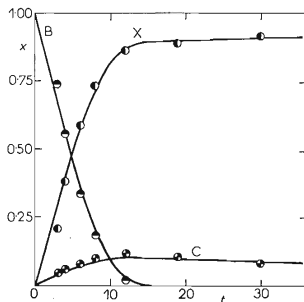


FIG. 2

Concentration Dependence of Reaction Components on Time at Hydrogenation of 4-Ethylcyclohexene on Pd/C at 20°C

analytically 4-ethylcyclohexene in the presence of 3-ethylcyclohexene and 1-ethylcyclohexene in the presence of ethylidencyclohexane these pairs were denoted in the same manner. Moreover the first two olefines are denoted as 4-ethylcyclohexene and the second two as 1-ethylcyclohexene.

Characteristic examples of the concentration dependences on time at hydrogenation of 4-vinylcyclohexene and the respective reaction intermediates are given in Figs 1–4. From Figs 1–3 it is obvious, that the concentration dependences are characteristic for the consecutive parallel reactions of zero order in respect to 4-vinylcyclohexene (Fig. 1), 4-ethylcyclohexene (Figs 1, 2), and vinylcyclohexane (Fig. 3). This was verified experimentally by measuring the initial reaction rates at different initial concentrations of the hydrogenated component. For hydrogenation of 1-ethylcyclohexene was determined the order of the reaction (the obtained value was 0.55) with respect to olefine, which is also in agreement with the concentration dependence given in Fig. 4. From the concentration dependences at hydrogenation of 4-vinylcyclohexene and from the respective intermediates (4-ethylcyclohexene, vinylcyclohexane) were estimated values of the initial reaction rates ($k_1, k_2, k_3, k_4, k_6, k_7$). Value of the

TABLE I

Rate Constants of Hydrogenation and Isomerization (20°C; Hexane)

Constant	k_1	k_2	k_3	k_4	k_5	k_6	k_7
Value mmol g _{cat} ⁻¹ min ⁻¹	0.503	3.55	1.19	0.143	0.33	2.3	3.64

TABLE II

Adsorption Constants of Hydrogenation and Isomerization (20°C; Hexane)

Reactant	K_1 l/mol ⁻¹	Reactant	K_1 l/mol ⁻¹
4-Vinylcyclohexene (A)	404	1-Ethylcyclohexene (C ₁)	6.8
Vinylcyclohexane (D)	404 ^a	Ethylidencyclohexane (C ₂)	6.8 ^a
4-Ethylcyclohexene (B)	54.3	Ethylcyclohexane (X)	0 ^a
3-Ethylcyclohexene (B)	54.3 ^a		

^a Expected values (see assumptions a), b), c)).

rate constant of 1-ethylcyclohexene (k_5) was determined from the linearized form of the kinetic equation

$$C_C^0/r^0 = C_C^0/k_5 + (k_5 K_C)^{-1}. \quad (8)$$

Values of the estimated rate constants are given in Table I. From the linearized Eq. (8) for hydrogenation of 1-ethylcyclohexene was also determined the value of the adsorption constant K_C . Ratios of adsorption constants (K_A/K_B and K_B/K_C) were estimated from the composition of the reaction mixture at hydrogenation of 4-vinylcyclohexene in the moment of concentration maximum of the respective intermediates. Values of K_A and K_B (Table II) were determined from the known absolute value of the adsorption constant K_C . The system of differential equations for individual reaction steps was solved by use of values of the rate and adsorption constants (Table I and II). For this solution has been necessary to accept the additional simplifying assumptions: a) adsorption of 4-vinylcyclohexene and vinylcyclohexane is basically affected by the vinyl group in the molecule and thus it has been assumed that their adsorption values are equal. b) 4-Vinylcyclohexene and 3-ethylcyclohexene have the same adsorption constant and are hydrogenated with the same rate to ethylcyclohexane. c) Ethylidencyclohexane and 1-ethylcyclohexene have the same adsorption constant and are hydrogenated to ethylcyclohexane with a comparable rate. The calculated concentration dependences are in Figs 1–4 represented by solid lines. The calculated concentration dependences and experimental points are in a very good agreement. In Fig. 1 is in detail plotted, as a dashed line, the calculated concentration dependence of vinylcyclohexane that was not analytically determined in the reaction mixture due to a very low maximum concentration of vinylcyclohexane (0.036). From the agreement of the calculated and experimental concentration dependences follows that the whole reaction system may be described by the Langmuir and Hinshelwood equations and that the made assumptions satisfy the studied system.

FIG. 3
Concentration Dependence of Reaction Components on Time at Hydrogenation of Vinylcyclohexane on Pd/C at 20°C

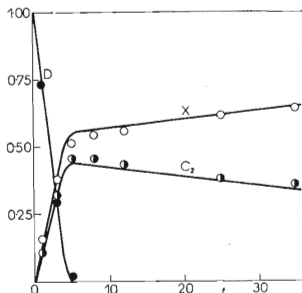


TABLE III
Comparison of Reactivities of Substituted Double Bonds

Type of bond	Rate constant $\cdot 10^3$ $\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$
$\text{CH}_2=\text{CH}-$	3.6
$-\text{CH}=\text{CH}-$	0.5-1.2
$-\text{CH}=\text{C}<$	0.33

Reactivities of olefines at competitive hydrogenation with 4-vinylcyclohexene.
At hydrogenation of 4-vinylcyclohexene were hydrogenated olefines with a double bond mono-, di- and tri-substituted. From kinetic measurements of 4-vinylcyclohexene, vinylcyclohexane, 4-ethylcyclohexene and 1-ethylcyclohexene reactivities of double bonds substituted in different way can be compared (Table III). From this table is obvious that the reactivity of olefines at hydrogenation decreases with the increasing number of substituents on the double bond²¹. From Table II follows that the degree of substitution of the double bond affects sorption of individual olefines on the used catalyst as well. With increasing substitution of the double bond decreases simultaneously the adsorption ability of olefines (expressed by the adsorption constant).

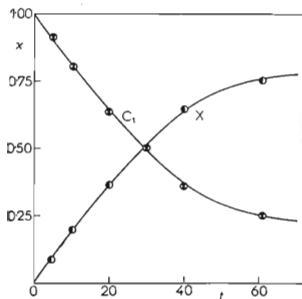


Fig. 4

Concentration Dependence of Reaction Components on Time at Hydrogenation of 1-Ethylcyclohexene on Pd/C at 20°C

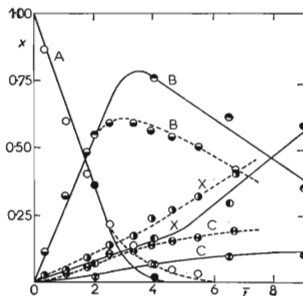


FIG. 5

Comparison of Hydrogenations of 4-Vinylcyclohexene on Catalysts of Two Particle Sizes (0.04 and 1.2-1.5 mm)

Isomerization of the olefines studied. A great influence of instability of olefines on hydrogenation selectivity is obvious from Figs 2 and 3 with the use of a catalyst having isomerization properties such as the used palladium catalyst. If the reaction selectivity is defined as the ratio of rate constants of hydrogenation and isomerization it has a value 1.58 for hydrogenation of vinylcyclohexane and value 8.58 for hydrogenation of 4-ethylcyclohexene. From these values follows that the reaction selectivity in relation to hydrogenation is the greater the more stable²⁰ is the hydrogenated olefine.

Effect of size of the catalyst particles. For hydrogenation of 4-vinylcyclohexene was also used the size of catalyst particles in the range 1.2 to 1.5 mm. The catalyst was situated in a mesh basket by which the reaction mixture was intensively mixed. Comparison of hydrogenations of 4-vinylcyclohexene on the catalyst with the particle size less than 0.04 mm and with the particle size in the range 1.2 to 1.5 mm is presented in Fig. 5. The time coordinate \bar{t} was for the measurements with the greater particle size calculated according to the relation

$$\bar{t} = tk_v/k_m,$$

where k_v is the rate constant for the particle size 1.2–1.5 mm and k_m for the particle size smaller than 0.04 mm.

The fraction of active internal catalyst surface was calculated for the catalyst with the greater particle size as 4.4% which corresponded to the assumption that 100% of the catalyst surface was active in the kinetic region on the powdery catalyst. From Fig. 5 for hydrogenation on greater particle size is obvious the decrease of the maximum concentration of 4-ethylcyclohexene and an concentration increase of 1-ethylcyclohexene and ethylcyclohexene as compared with the hydrogenation in the kinetic region as concerns the internal diffusion. The selectivity of reaction varies with the use of the greater particle size where the effect of internal diffusion of components varies. To explain this phenomena it is possible to accept the hypothesis according to which those reaction steps are preferred in which hydrogen does not participate (isomerization) as compared with hydrogenation. In the case the effect of internal diffusion is not negligible the hydrogen concentration inside the catalyst particle is low and thus isomerization can take place when compared with hydrogenation. These results are in agreement with the study of the effect of hydrogen pressure on selectivity of hydrogenation of 1-hexene²².

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LIST OF SYMBOLS

C_i	concentration of component i (mol cm^{-3})
C_i^0	initial concentration of component i (mol cm^{-3})
k_i	rate constant of the i -th reaction step ($\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$)
K_i	adsorption constant of component i (l mol^{-1})
r_i^0	initial reaction rate ($\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$)
t	time (s)
V	volume of the reaction mixture (cm^3)
W	amount of catalyst (g_{cat})
$x_i = C_i/C_A^0$	relative concentration of component i

REFERENCES

- De Ruiter E., Jungers J. C.: Bull. Soc. Chim. Belges 58, 210 (1949).
- Coussement F., Jungers J. C.: Bull. Soc. Chim. Belges 59, 295 (1950).
- Červený L.: *Thesis*. Institute of Chemical Technology, Prague 1969.
- Červený L., Růžička V.: This Journal 34, 1560 (1969).
- Sporka K., Hanika J., Růžička V., Vostrý B.: This Journal 37, 52 (1972).
- Lebedev S. V., Sergienko S. R.: Ž. Obšč. Chim. 5, 1839 (1935).
- Tepenicyna B. P., Farberov M. I., Dorogova N. K.: Neftechimija 3, 876 (1963).
- Frejdlin L. C., Plate A. F., Belikova A. N.: Neftechimija 4, 382 (1964).
- Tabler D. C. (Phillips Petroleum Co.): U.S.-Pat. 3 546 307 (1970).
- Zapletal V., Soukup J., Růžička V., Kolomazník K.: This Journal 33, 2436 (1968).
- Pouček J.: *Thesis*. Institute of Chemical Technology, Prague 1971.
- Berlande A.: Bull. Soc. Chim. France 9, 642 (1942).
- Tříška J.: *Thesis*. Institute of Chemical Technology, Prague 1968.
- Zapletal V., Soukup J., Růžička V., Mistrík E. J.: Czechoslov. Pat. 111 791 (1964).
- Růžička V., Zapletal V., Soukup J.: Czechoslov. Pat. 91 868 (1959).
- Sporka K., Hanika J., Růžička V.: Chem. listy 65, 1209 (1971).
- Červený L., Hanika J., Růžička V.: Chem. průmysl 20, 9 (1970).
- Hanika J., Sporka K., Růžička V., Deml J.: This Journal 37, 951 (1972).
- Lapidus L.: *Digital Computations for Chemical Engineers*. McGraw-Hill, New York 1962.
- Herling J., Shaptai J., Gil-Av E.: J. Am. Chem. Soc. 87, 4107 (1965).
- Červený L., Růžička V.: This Journal 34, 1570 (1969).
- Červený L., Zapletal V., Růžička V.: Chem. průmysl 20, 160 (1970).

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