

KINETICS OF HYDROGENATION OF CYCLIC BUTADIENE OLIGOMERS ON PALLADIUM CATALYSTS. CYCLOOCTADIENE ISOMERS

Jiří HANIKA, Ivan SVOBODA and Vlastimil RŮŽIČKA

Department of Organic Technology,

Prague Institute of Chemical Technology, 166 28 Prague 6

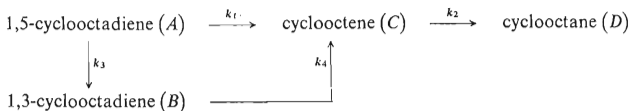
Received July 3rd, 1980

Kinetics of hydrogenation of 1,3- and 1,5-cyclooctadiene and cyclooctene on palladium support catalysts (Pd/CaCO₃, Pd/γ-Al₂O₃) were measured in heptane solutions at 300 K and atmospheric pressure of hydrogen. The kinetic constants were obtained by relating the experimental data to a kinetic model in which the partial reactions are assumed to be 1st order.

Hydrogenation of cyclic oligomers of 1,3-butadiene — 1,5-cyclooctadiene and 1,5,9-cyclododecatriene — is one of the basic steps in the synthesis of C₈ or C₁₂ lactams, dicarboxylic acids and their derivatives, which are promising products of organic synthesis. The present work is concerned with the kinetics of hydrogenation of 1,5- and 1,3-cyclooctadiene and of 1,5,9-cyclododecatriene stereoisomers (see p. 1039) on commercial palladium catalysts in liquid phase at 300 K and atmospheric pressure of hydrogen.

Hydrogenation of 1,5-cyclooctadiene has been investigated using heterogeneous palladium¹⁻⁸, copper⁹, and nickel¹⁰⁻¹⁴ catalysts. Most authors have concentrated on selective preparation of cyclooctene, the intermediate product of the reaction. The kinetics of the reaction has been examined in our previous works^{15,16}; the experimental data have been related to a 1st order kinetic model (hydrogenation on a Pd/Al₂O₃ catalyst in methanolic solution) and to kinetic equations of the Langmuir-Hinshelwood type (hydrogenation on a Pd/C catalyst in cyclooctane solution). In the present work, data obtained on various palladium catalysts commercially produced in Czechoslovakia and on Lindlar's catalyst, product of Engelhard, Great Britain, are evaluated and mutually compared.

Hydrogenation of 1,5-cyclooctadiene has been observed¹⁵ to be associated with migration of the double bond to give 1,3-cyclooctadiene. In this work, the following reaction scheme for hydrogenation of 1,5-cyclooctadiene has been therefore adopted:



This scheme includes also hydrogenation of 1,3-cyclooctadiene in which the 1,5 isomer is absent from the reaction mixture. For a constant volume of the reaction mixture and constant hydrogen pressure, the following system of equations can be written for hydrogenation of 1,5-cyclooctadiene in a discontinuous, isothermal, stirred reactor*

$$dC_A/dt = -(k_1 + k_3) C_A \quad (1)$$

$$dC_B/dt = k_3 C_A - k_4 C_B \quad (2)$$

$$dC_C/dt = k_1 C_A + k_4 C_B - k_2 C_C \quad (3)$$

$$C_D = C_A^0 - C_A - C_B - C_C \quad (4)$$

with the initial conditions

$$t = 0, \quad C_A = C_A^0, \quad C_B = C_C = C_D = 0. \quad (5)$$

For hydrogenation of 1,3-cyclooctadiene, the kinetic relations are analogously

$$dC_B/dt = -k_4 C_B \quad (6)$$

$$dC_C/dt = k_4 C_B - k_2 C_C \quad (7)$$

$$C_D = C_B^0 - C_B - C_C \quad (8)$$

$$t = 0, \quad C_B = C_B^0, \quad C_C = C_D = 0. \quad (9)$$

The systems of differential equations were solved numerically by using the Runge-Kutta-Merson¹⁷ method on Tesla 270 and Tektronic 4051 computers. The requisite programs were set up in the Fortran and Basic languages. The precision was chosen 10^{-4} , an integration step took 30 s. Graphical comparison of the experimental data with the numerical solution was used to determine the most probable values of the partial reactions rate constants by means of the shooting method. An efficient identification of the model parameters was facilitated by the use of the Tektronix 4631 video display, on which the solution could be shown graphically.

EXPERIMENTAL

Chemicals

1,5-*cis,cis*-Cyclooctadiene puriss. (Koch-Light, Colnbrook), b.p. 151°C/0.1 MPa, $n_{25} 1.4905$. 1,3-*cis,cis*-Cyclooctadiene pract. (Fluka, Buchs). *cis*-Cyclooctene was prepared¹⁸ by selective

* See the appended list of symbols.

hydrogenation of 1,5-cyclooctadiene using palladium on γ -alumina as the catalyst; b.p. 138°C/0.1 MPa, n_{20} 1.4470. Cyclooctane was prepared¹⁹ by hydrogenation of 1,5-cyclooctadiene using Raney-nickel catalyst; b.p. 149°C/0.1 MPa, n_{20} 1.4587. n-Heptane (Jenapharm-Laborchemie, Apolda, or Lobs-Chemie, Wien); b.p. 98.4°C/0.1 MPa; vapour pressure 6.43 kPa at 300 K. Hydrogen technical, quality B, electrolytical (Technoplyn, Prague).

Catalysts

Cherox 40—00 (0.56% palladium on γ -alumina) Chemopetrol CHZ ČSSP, Litvínov); pellets 5 mm in diameter were crushed and screened prior to use (grain size below 0.05 mm). Lindlar's catalyst (Engelhard, Great Britain), grain size below 0.05 mm. Lindlar's catalyst (5% palladium on calcium carbonate) (Farmakon, Olomouc), grain size below 0.05 mm.

Apparatus and Procedure

1 ml of the substrate in 25 ml solution in n-heptane was hydrogenated at 300 K and atmospheric pressure using 0.2—1 g of palladium catalyst. The experiments were conducted in the discontinuous isothermal stirred reactor described — along with the procedure — in paper²⁰. In all experiments the reaction proceeded in the kinetic region as concerns the mass transfer between the various system phases, as defined in²¹. External mass transfer was prevented by vigorous stirring (9 Hz), the effect of internal diffusion was eliminated by choosing catalyst with suitably small grain size ($d_p < 0.05$ mm).

The reactor was connected to a system of thermostated volumetric gas burettes, from which hydrogen was fed into the reactor in such a manner that a constant (atmospheric) pressure was held in the apparatus. The reaction rate or degree of conversion was measured by periodically reading the volume of hydrogen in the burettes. The dependences of the reaction rates on time were extrapolated to give the initial hydrogenation rates, which were then corrected for changes in the atmospheric pressure under the assumption that the reaction is 1st order with respect to hydrogen.

From series of hydrogenations to a known degree of conversion, determined from the amount of hydrogen reacted and from analyses of the reaction mixtures, time dependences were obtained for the concentrations of the reaction products of 1,3- and 1,5-cyclooctadiene; these were evaluated to give the initial estimates of the rate constants.

The maximum error in the determination of the degree of conversion did not exceed 2% rel., the average error in the determination of the initial reaction rate from the time dependence of the composition was about 10% rel. The experiments were several times repeated.

Analyses

The reaction mixture samples were analyzed gas-chromatographically on a CHROM 2 apparatus (Laboratorní přístroje, Prague) with flame ionization detection under the following conditions¹⁸: glass column 9 m long, inner diameter 2.5 mm; column packing: 15% polyethylene glycol 6000 on Chromaton N-AW-DMCS (grain size 0.2—0.5 mm); carrier gas: nitrogen, overpressure 0.14 MPa; hydrogen flow rate $8.1 \cdot 10^{-3}$ mol min⁻¹, air flow rate 10 ml min⁻¹; working temperature 80°C, sensitivity 1 : 20, quantity analyzed: 1 μ l of the hydrogenation mixture, the catalyst was separated by sedimentation. The relative retention times: cyclooctane 1.00, cyclooctene 1.11, 1,3-cyclooctadiene 1.41, 1,5-cyclooctadiene 1.83. In the concentration region of the reaction products analyzed, the percentage proportions of the areas of the chromatographic peaks were

found to correspond, within the limits of error, to the sample composition in weight per cent. With regard to the regular shape of the chromatographic peaks, the areas were determined by the triangulation method. The error of determination was 5% rel.

RESULTS AND DISCUSSION

Catalytic activity of the catalysts. The palladium catalysts were first compared as to their activity for hydrogenation of unsaturated hydrocarbons with eight-membered ring. A survey of the initial hydrogenation rates on the various catalysts is presented in Table I. The rates of hydrogenation of cyclooctadiene isomers and cyclooctene are seen to differ considerably; the Lindlar's catalyst and palladium on alumina are obviously highly selective for saturation of only one of the two double bonds in the cyclooctadiene molecule. Selectivity of hydrogenation of 1,5-cyclooctadiene can be seen in Fig. 1, showing the dependence of the hydrogenation rate on the degree of conversion for all the catalysts tested. At the degree of conversion 0.5, the shape changes sharply, owing to the vanishing of 1,5-cyclooctadiene from the reaction mixture, the following hydrogenation of cyclooctene being essentially slower. Somewhat faster was the hydrogenation of cyclooctene on the Pd/C catalyst; also, this catalyst was least selective for partial hydrogenation of only one double bond in the cyclooctadiene molecule yielding cyclooctene. A similar result was obtained from hydrogenation of 1,3-cyclooctadiene. In the case of the Pd/Al₂O₃ catalyst, 1,3-cyclooctadiene was hydrogenated 3.5 times faster than 1,5-cyclooctadiene probably owing to the favourable effect of the double bond conjugation in the former isomer.

Kinetics of hydrogenation of 1,3-cyclooctadiene. The variations in the reaction mixture composition during hydrogenation of 1,3-cyclooctadiene on Lindlar's and on Pd/Al₂O₃ catalysts are shown in Figs 2 and 3, respectively. The experimental points are always averages of several independent experiments, the curves represent the solution of the system of equations (6)–(9) with the most probable rate constants

TABLE I
Initial Rates of Hydrogenation of the Hydrocarbons Used (mmol H₂/min g_{cat})

Reactant	Pd/Al ₂ O ₃	Pd/C	Pd/CaCO ₃
1,3-Cyclooctadiene	9.78	4.91	1.15
1,5-Cyclooctadiene	2.70	3.35	1.83 (1.39 ^a)
Cyclooctene	0.069	—	0.034

^a Lindlar's catalyst of Engelhard.

TABLE II
Values of the Rate Constants of the Partial Reactions (300 K)

Catalyst	Reactant ^a	Rate constant, min ⁻¹ g _{cat} ⁻¹			
		<i>k</i> ₁	<i>k</i> ₂	<i>k</i> ₃	<i>k</i> ₄
Pd/CaCO ₃ (Farmakon)	1,3-COD	—	0.0040	—	0.38
	1,5-COD	0.30	0.0044	0.08	0.38
	CEN	—	0.0052	—	—
Pd/CaCO ₃ (Engelhard)	1,5-COD	0.40	0.0044	0.10	0.38
Pd/Al ₂ O ₃	1,3-COD	—	0.0080	—	1.5
	1,5-COD	0.56	0.0088	0.18	1.5
	CEN	—	0.0085	—	—
Pd/Al ₂ O ₃ ^b	1,5-COD	0.19	0.003	0.17	1.1
	CEN	—	0.008	—	—

^a 1,3-COD 1,3-cyclooctadiene, 1,5-COD 1,5-cyclooctadiene, CEN cyclooctene; ^b ref.¹⁵.

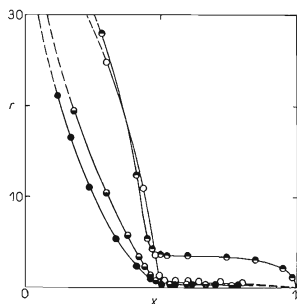


FIG. 1

Dependence of the Rate of Hydrogenation of 1,5-Cyclooctadiene on the Conversion

Catalyst (0.5 g): ○ Pd/Al₂O₃, ● Pd/C, ● Pd/CaCO₃ (Farmakon), ● Pd/CaCO₃ (Engelhard).

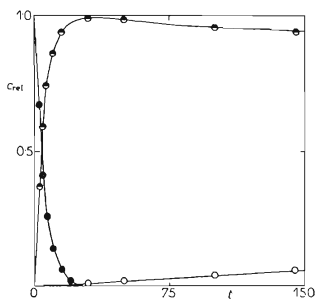


FIG. 2

Hydrogenation of 1,3-Cyclooctadiene

Catalyst: 0.5 g Pd/CaCO₃ (Farmakon); ● 1,3-cyclooctadiene, ● cyclooctene, ○ cyclooctane.

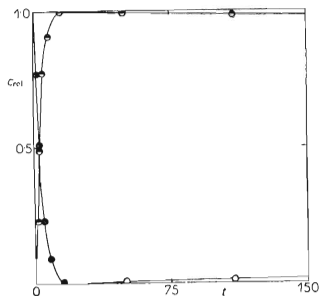


FIG. 3

Hydrogenation of 1,3-Cyclooctadiene

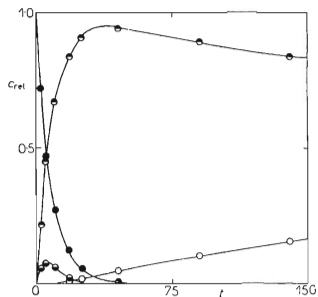
Catalyst: 0.1 g Pd/ γ -Al₂O₃; for point designation see Fig. 2 caption.

FIG. 4

Hydrogenation of 1,5-Cyclooctadiene

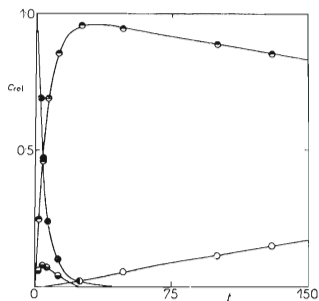
Catalyst: 0.5 g Pd/CaCO₃ (Farmakon);
● 1,5-cyclooctadiene, ◐ 1,3-cyclooctadiene,
◑ cyclooctene, ○ cyclooctane.

FIG. 5

Hydrogenation of 1,5-Cyclooctadiene

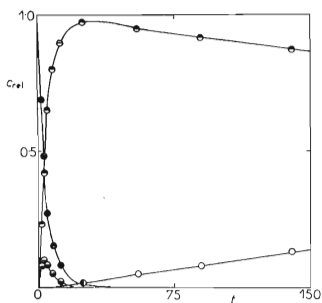
Catalyst: 0.5 g Pd/CaCO₃ (Engelhardt);
for point designation see Fig. 4 caption.

FIG. 6

Hydrogenation of 1,5-Cyclooctadiene

Catalyst: 0.5 g Pd/ γ -Al₂O₃; for point designation see Fig. 4 caption.

of the partial hydrogenations. In Table II the rate constant values are compared with one another and with those for hydrogenation of 1,5-cyclooctadiene. The kinetic data measured are characteristic by the high and flat maximum for the concentration of cyclooctene, due to the considerably lower rate of hydrogenation of this intermediate. The rate constants for cyclooctene hydrogenation determined from the data of hydrogenation of 1,3-cyclooctadiene agree well with those arrived at assuming that hydrogenation of cyclooctene itself obeys the 1st order kinetics (Table II).

Kinetics of hydrogenation of 1,5-cyclooctadiene. The 1,3-isomer has been found to be present in the reaction mixture during the hydrogenation of 1,5-cyclooctadiene. The migration of the double bonds is obviously induced by the strain in the eight-membered ring with two double bonds and the tendency to form a system of conjugated double bonds. This process necessarily involves formation of the 1,4 isomer, which, however, was not available; in view of the occurrence of isolated double bonds in the 1,4 and 1,5 isomers, however, no great differences are to be expected between the properties (retention volumes, reactivity) of the two isomers. In the data handling, the occurrence of the 1,5- and 1,3-cyclooctadiene isomers only was therefore assumed. The dependence of the reaction mixture composition on the hydrogenation period for 1,5-cyclooctadiene is shown in Figs 4–6 for three different catalysts. The experimental values were again related to the numerical solution of the pertinent kinetic equations (1)–(5); the most probable values of the rate constants are given in Table II. On the whole, the constants of the partial reaction steps obtained for hydrogenation of 1,5-cyclooctadiene, 1,3-cyclooctadiene, and cyclooctene are in a very good mutual agreement. The results also indicate that the rate of hydrogenation of 1,5-cyclooctadiene on the catalysts in question is 3–4 times higher than the rate of isomerization. The highest selectivity for hydrogenation of 1,5-cyclooctadiene to cyclooctene was attained on the Pd/Al₂O₃ catalyst. Lindlar's catalyst of Farmakon is somewhat more active than the product of Engelhard, the selectivity of the two catalysts for the formation of cyclooctene being roughly equal. In Table II, the rate constants found are also compared with our previous results¹⁵ concerning kinetics of hydrogenation of 1,5-cyclooctadiene in methanolic solution also at atmospheric pressure of hydrogen and 20°C. The results indicate that the more polar solvent – methanol – favours the double bond migration, as the isomerization rate constant-to-hydrogenation rate constant ratio is $k_3/k_1 = 1$, whereas in the case of heptane this ratio is only 0.3.

Conclusion. Generally, hydrogenation of the two cyclooctadiene isomers on the catalysts tested is selective. The reaction system can be well described by a kinetic model in which the partial reaction steps are 1st order. The low rate of hydrogenation of the intermediate product – cyclooctene – makes it possible to obtain this compound in the reaction mixture in 97–99% contents.

LIST OF SYMBOLS

C	concentration (mol l^{-1})
C^0	initial concentration (mol l^{-1})
$C_{\text{rel}} = C/C^0$	concentration (-)
k_i	rate constant ($\text{min}^{-1} \text{g}_{\text{cat}}^{-1}$)
r^0	initial rate ($\text{mol H}_2 \text{ min}^{-1} \text{g}_{\text{cat}}^{-1}$)
t	time (min)
T	temperature (K)

REFERENCES

- Hill J. W.: J. Amer. Chem. Soc. 52, 4110 (1930).
- Neunhoeffer O., Pasche P.: Ber. Deut. Chem. Ges. 728, 919 (1939).
- Feagar R. A., Copenhauer J. E.: J. Amer. Chem. Soc. 62, 869 (1940).
- Coffman R. D., Berchet C. J., Peterson W. R., Spanagel E. W.: J. Polymer Sci. 2, 306 (1947).
- Stacey M., Bourne E. J., Tallow J. C., Tedler J. M.: Nature (London) 164, 705 (1949).
- Magee P. S. (California Research Co): Fr. 1 318 312 (1963).
- Piccles W. (Geigy Ltd.): Brit. 1 046 780 (1966).
- Hayes W. K. (Columbian Carbon Co.): U.S. 3 418 386 (1968).
- Unilever N. V.: Neth. 6 608 993 (1966).
- Chappel S. F. (Cities Service Res. Develop. Co.): Belg. 64 3763 (1964).
- Columbian Carbon Co: Brit. 1 023 499 (1966).
- Zuech E. A. (Philips Petroleum Co.): U.S. 3 493 625 (1970).
- Nowack G. P., Johnson M. M.: U.S. 3 637 877.
- Nowack G. P.: U.S. 3 636 175.
- Hanika J., Sporka K., Růžička V.: Sb. Vys. Šk. Chemicko-Technol. Praze C 23, 47 (1976).
- Hanika J., Vychodil P., Růžička V.: Chem. Prům. 27, 449 (1977).
- Lapidus L.: *Digital Computations for Chemical Engineers*. McGraw Hill, New York 1962.
- Chlumská J.: *Thesis*. Prague Institute of Chemical Technology, Prague 1978.
- Hanika J., Sporka K., Kráčmar L., Růžička V.: Chem. Prům. 30, 31 (1980).
- Soukup J., Zapletal V.: Chem. Listy 62, 991 (1968).
- Červený L., Hanika J., Růžička V.: Chem. Prům. 20, 9 (1970).

Translated by P. Adámek.