INVESTIGATION OF HYDROGENATION IN LIQUID PHASE. XIX.*
KINETICS OF CONSECUTIVE REACTIONS DURING THE HYDROGENATION OF 2-METHYL-3-BUTYNE-2-OL

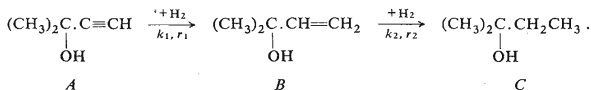K.Sporka, J.Hanika, V.Růžička and B.Vostrý

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

The kinetics of consecutive reactions was studied during the hydrogenation of hexane solutions of 2-methyl-3-butyne-2-ol on a palladium catalyst in the liquid phase in the temperature range 12—30°C. The measurements were performed at an atmospheric pressure in an isothermal and half-flow reactor agitated by a rotating stirrer. By measuring the dependence of the initial reaction rate on the initial concentration of a substrate separately for both reactions, the reaction orders with respect to both substrates were determined. From the temperature dependences of the rate constants, the activation energies of single reaction steps were calculated. On the basis of the experimental measurements, the ratios of the adsorption constants of the reactant and the reaction intermediate were estimated as well as the reaction selectivity which decreased with increasing temperature.

The aim of the present work was a study of the kinetics and selectivity of consecutive reactions in the liquid phase. Of industrial importance is for example the selective hydrogenation of acetylene compounds contained in hydrocarbon fractions $(C_3 - C_5)^{1-3}$. This process is usually performed in the liquid phase in trickle bed reactors. For the study of consecutive reactions the hydrogenation of 2-methyl-3-butyne-2-ol was chosen, which proceeds on a palladium catalyst according to:

$$(CH_3)_2C.C{\equiv}CH \xrightarrow[k_1, r_1]{\cdot + H_2} (CH_3)_2C.CH{=}CH_2 \xrightarrow[k_2, r_2]{+ H_2} (CH_3)_2C.CH_2CH_3 .$$
$$\quad\ \ \overset{|}{OH} \qquad\qquad\qquad\quad \overset{|}{OH} \qquad\qquad\qquad\qquad \overset{|}{OH}$$
$$\qquad A \qquad\qquad\qquad\qquad\quad B \qquad\qquad\qquad\qquad\qquad C$$

This reaction was studied[4] in connection with the possibility to use the reaction intermediate **B** for the production of isoprene[5]. Karapetjan and coworkers[4] measured only the influence of compounds of a basic character on the hydrogenation selectivity neglecting kinetic aspects.

THEORETICAL

Assuming that it is plausible to use the kinetic equations of the Hougen–Watson type[6], it is possible to express the time changes of the reaction components in a discontinuous agitated system by the equations:

$$-\frac{V}{W}\frac{dc_A}{dt} = \frac{k_1 K_A c_A}{1 + K_A c_A + K_B c_B + K_C c_C + K_1 c_1}, \qquad (1)$$

$$\frac{V}{W}\frac{dc_B}{dt} = \frac{k_1 K_A c_A - k_2 K_B c_B}{1 + K_A c_A + K_B c_B + K_C c_C + K_1 c_1}, \qquad (2)$$

$$\frac{V}{W}\frac{dc_C}{dt} = \frac{k_2 K_B c_B}{1 + K_A c_A + K_B c_B + K_C c_C + K_1 C_1}, \qquad (3)$$

with the boundary conditions:

$$t = 0; \quad c_A = c_{A_0}; \quad c_B = c_C = 0. \qquad (4)$$

In Eqs $(1)-(3)$ the concentration of hydrogen dissolved in the reaction mixture is not given explicitly, as it is a constant during the measurement (it is equal to an equilibrium value at a given pressure and temperature) and it is thus comprised in the rate constants k_1, k_2. For a strong adsorption ability of compounds with multiple bonds on the catalyst surface[7] it is possible to neglect the term $\left(1 + K_C c_C + K_1 c_1\right)$ in Eqs $(1)-(3)$ against the term $\left(K_A c_A + K_B c_B\right)$. During the initial stage of the hydrogenation *i.e.* $c_B \to 0$ it is acceptable to adopt the zeroth reaction order with respect to the concentration of reactant A. The same situation arises during the isolated hydrogenation of the compound $B(c_A = 0)$. The integration of Eqs $(1)-(3)$ would be very involved, however, by eliminating t a substantial simplification results

$$- dc_B/dc_A = (k_1 K_A c_A - k_2 K_B c_B)/k_1 K_A c_A. \qquad (5)$$

Eq. (5) must be accompanied by the boundary condition

$$c_A = c_{A_0}; \quad c_B = 0. \qquad (6)$$

Differential Eq. (5) integrates easily[8] yielding a dependence of the concentration of the intermediate B on the reactant A concentration expressed by the relation:

$$c_B = \frac{q}{q-1} c_{A_0}^{(q-1)/q} c_A^{1/q} + \frac{q}{1-q} c_A, \qquad (7)$$

where

$$q = k_1 K_A/k_2 K_B. $$

The value of the parameter q could be determined either directly from the dependence of the intermediate concentration on the reactant concentration or from the ratio of the concentrations of the components A and B at the maximum concentration of the intermediate B for which it holds

$$dc_B/dc_A = 0 . \tag{8}$$

From Eq. (8) we may obtain:

$$q = c_B^{(max)}/c_A^{(max)} = k_1 K_A/k_2 K_B . \tag{9}$$

EXPERIMENTAL

Chemicals

2-Methyl-3-butyne-2-ol of the n.b.p. 102—103°C was prepared by the reaction[9] of acetone with sodium acetylide. The n.b.p. of pure 2-methyl-3-butene-2-ol (Koch-Light, Great Britain) was 97°C. 2-Methyl-2-butanol was prepared by the hydrogenation of 2-methyl-3-butene-2-ol on a W4 Raney-nickel catalyst[10], n.b.p. 102·5°C. The n.b.p. of 2-methyl-1-propanol, A.R. grade (Lachema was 108·4°C; hexane, A.R. grade (Lachema), n.b.p. 69°C; tetrachloromethane, pure grade (Lachema), n.b.p. 76·5°C. Hydrogen was of the technical electrolytic B grade (Technoplyn, Pardubice). As a catalyst, 3 wt. % palladium was used on a narrow pore active carbon (cylinders of the diameter 4·2 mm), the product No 9041 (Chemické závody ČSSP, Záluží). The granulation of the catalyst was 0·04—0·07 mm during all experiments.

Apparatus and Method

The apparatus scheme is depicted on Fig. 1. The glass reactor[11] was placed in a thermostat and the agitation of the reaction mixture was performed by a blade stirrer which made it possible to change continuously the stirring frequency $(0—1500 \text{ min}^{-1})$. A detailed description of the measuring apparatus is given in another paper[11].

The kinetic measurements were made at an atmospheric pressure in the temperature range 12—30°C. The reactor temperature was maintained by an ultrathermostat with a $\pm 0\cdot1$°C accuracy. Into the reactor fixed in the thermostat it was successively added 0·2 g of the catalyst, 100 ml hexane, and 0·5 ml 2-methyl-1-propanol (an internal standard for the analytical determination). The reactor was closed, the stirrer switched on, and the feeding of the reactor with hydrogen was started. The catalyst was activated during 30 min at a hydrogen flow rate of 70 ml/min and at the agitation frequency 600 min^{-1}. After the activation had been finished, the agitation frequency was increased to 1200 min^{-1} and the hydrogen flow rate decreased to 50 ml/min. After the hydrodynamic regime had reached a steady state, 1 ml of 2-methyl-3-butyne-2-ol was injected through the orifice for withdrawing samples at the time $t = 0$. The samples for the analysis were withdrawn by a hypodermic syringe in 5 min time intervals. The experiments at single temperatures were repeated five times on the whole.

Analysis

The method of determining all reaction components was taken over from another work[4]. The analysis was made gas chromatographically on a Chrom-1 apparatus (Laboratorní přístroje

Prague) with a flame-ionization detection. Working conditions: stationary phase 10% poly (ethylene glycol) on Chromaton N (Lachema, Brno); length of the stainless column 3·2 m (inner diameter 5 mm); temperature 70°C; carrier gas nitrogen (flow rate 4 ml/min); hydrogen flow rate 10·5 ml/min; sample amount 10 μl. The evaluation of chromatograms was made by the method of the internal standard, in our case 2-methyl-1-propanol was used.

RESULTS AND DISCUSSION

Kinetic measurements. The measurements were performed in the kinetic region with respect to the diffusional transfer of the reaction components to the outer surface of the catalyst grain, *i.e.* at such hydrodynamical conditions in the reactor for which the reaction rate did not depend on the agitation intensity[11]. Experimentally it was verified that the reaction rate in the given arrangement did not depend on the way of hydrogen feeding (below or above the level of the reaction mixture) and on the hydrogen flow rate in the region $30-100$ ml/min. The influence of the internal diffusion was excluded by choosing a sufficiently fine granulation of the catalyst $(0·04-0·07$ mm) for which an effectiveness factor of 90% (ref.[12]) was measured during the hydrogenation of cyclohexene on the same catalyst. Hydrogenation rates of 2-methyl-3-butyne-2-ol and cyclohexene on the catalyst employed were comparable.
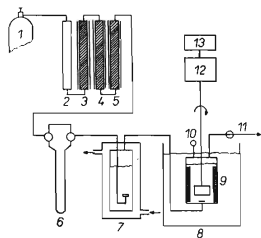

FIG. 1

Apparatus Scheme

1 Hydrogen pressure cylinder; *2* tube containing phosphoric acid on silica gel; *3* tube with the Ni/SiO$_2$ catalyst; *4* tube with the Cu/SiO$_2$ catalyst; *5* tube with the molecular sieve; *6* flow meter; *7* hydrogen saturator; *8* thermostat; *9* agitated reactor; *10* withdrawal of samples; *11* degassing; *12* engine; *13* contactless revolution counter.
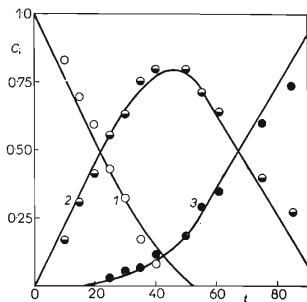

FIG. 2

Time Dependence of the Concentrations of the Components during Hydrogenation 2-Methyl-3-butyne-2-ol at 12°C

1 2-Methyl-3-butyne-2-ol (A), *2* 2-methyl-3-butene-2-ol (B), *3* 2-methyl-2-butanol (C).

Calculation of the initial reaction rate. The reaction rate with regard to the hydro-. gen concentration was considered to be of the first order[7,13,14] and was not verified. The experimentally determined reaction order with regard to the substrate concentration was of the zeroth order in the region of the measurements and so the initial reaction rate may be expressed by the relation:

$$r_0 = k c_H . \tag{10}$$

The value of the hydrogen concentration in the reaction mixture at the temperature of the measurement was calculated from the relation:

$$c_H = c_H' \frac{(P_b - P^0)}{760} \exp\left[\frac{\Delta H}{R}\left(\frac{1}{T'} - \frac{1}{T}\right)\right]. \tag{11}$$

It was assumed during the measurements that the liquid phase properties were identical with those of the pure solvent due to low substrate concentrations in the liquid phase. The hydrogen solubility in hexane was taken from another work[16] and the heat of solution from the work[12]. The time dependence concentration of the components present in the reaction mixture is illustrated in Fig. 2. The full lines were obtained by a numerical integration of Eqs (1)−(3) on the assumption that the value
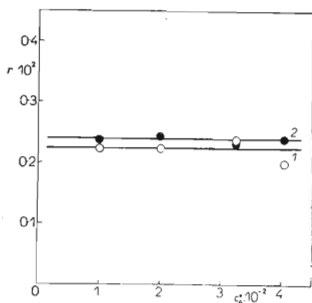

FIG. 3

Dependence of the Initial Reaction Rate on the Initial Concentration of the Substrate at 20°C

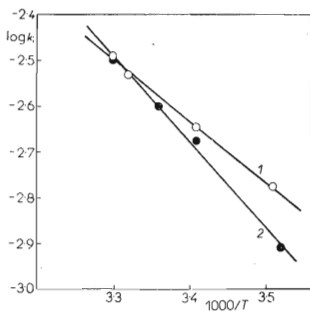*1* 2-Methyl-3-butyne-2-ol (A), *2* 2-methyl-3-butene-2-ol (B).

FIG. 4

Temperature Dependence of the Rate Constants of Both Reactions

1 2-Methyl-3-butyne-2-ol (A), *2* 2-methyl-3-butene-2-ol (B).

of the $\left(1 + K_C c_C + K_I c_I\right)$ term was negligible compared with the sum $\left(K_A c_A + K_B c_B + K_C c_C\right)$. The solution was carried out by a modified Runge–Kutta–Merson method on a NCR 4120 computer. The initial estimated values of the solution were: $k_1 = 2 \cdot 4 . 10^{-2}$; $k_2 = 1 \cdot 91 . 10^{-2}$; $K_A/K_B = 9 \cdot 9$. The values of the reaction constants k_1, k_2 and of the ratio K_A/K_B were obtained from several single measurements of the hydrogenation of 2-methyl-3-butyne-2-ol and 2-methyl-3-butene-2-ol at a given temperature. From the adduced figure it is obvious that the experimental points follow closely the calculated curves and that they exhibit a course characteristic for consecutive reactions of the zeroth order. The experimental course is atypical only during the initial reaction stage due probably to attaining the steady-state regime in the reaction system and therefore the values of the initial reaction rates were determined from the region of the linear course of the respective curve.

Determination of the reaction order. Both reaction steps were studied separately. The orders of the examined reactions were determined by measuring the dependence of the initial reaction rate on the initial concentration of the substrate. The resulting dependence is illustrated for both steps on Fig. 3 from which it is obvious that the orders of both reactions of the consecutive system are zero in the measured range of substrate concentrations.

Determination of activation energies. The activation energies were determined from the temperature dependences of the rate constants of the reactions. The second reaction (hydrogenation of the component B) was again studied separately. The resulting dependences are given for both reactions in Fig. 4 from which the values of the activation energies were read off on the basis of the Arrhenius relation as $6 \cdot 1$ kcal/mol for the hydrogenation $A \rightarrow B$ and $8 \cdot 7$ kcal/mol for the hydrogenation $B \rightarrow C$.
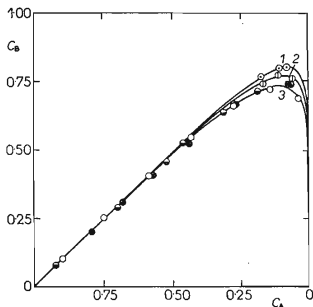

Fig. 5

Dependence of the Concentration of 2-Methyl-3-butene-2-ol (B) on the Concentration of 2-Methyl-3-butyne-2-ol (A)

1 12°C, *2* 20°C, *3* 30°C (three different experiments).

Estimation of adsorption constants. The hydrogenation experiments with 2-methyl-3-butyne-2-ol were evaluated on the basis of Eq. (*7*), *i.e.* of the dependence of the intermediate B concentration on the concentration of the reactant A. The respective dependence is represented in Fig. 5 for three different reaction temperatures. The full lines are theoretical curves (by Eq. (*7*)) with the value of q determined from Eq. (*9*). Experimental points from three experiments at 30°C are given for illustration in Fig. 5. (Experimental points for the other temperatures are shown in Fig. 5 only in the region of the respective maxima.)

From Eq. (*9*) and from the known ratios of the rate constants for single temperatures it was possible to read off the ratio of the adsorption constants K_A/K_B at the experimental temperatures. The values of the ratios of the adsorption constants are given in Table I.

TABLE I

Temperature Dependence of the Ratio of the Rate and Adsorption Constants

Abs. temp., K	Parameter q	k_1/k_2	K_A/K_B
285	12·5	1·26	9·9
293	10·0	1·11	9·0
303	7·5	0·96	7·8

From Table I it is further evident that the selectivity of the reaction decreases with increasing temperature (the value of the parameter q decreases). This result is in accordance with the experimentally determined values of the activation energies of single reaction steps as the value of the activation energy of the second reaction is higher than that of the formation of the intermediate B.

LIST OF SYMBOLS

c_i	concentration of the i-th component (mol cm^{-3})
c_H	hydrogen concentration in the liquid phase (mol cm^{-3})
$C_i = c_i/c_{A_0}$	relative concentration of the i-th component
ΔH	differential heat of solution (kcal mol^{-1})
k_i	rate constant of the i-th step (mol g$_{catalyst}^{-1}$ min^{-1})
K_i	adsorbtion coefficient of the i-th component (cm^3 mol^{-1})
P^0	saturated vapour pressure (Torr)

P_b atmospheric pressure (Torr)
q parameter, *cf.* Eq. (7)
r reaction rate (mol $g_{catalyst}^{-1}$ min^{-1})
R gas constant (kcal mol^{-1} deg^{-1})
t time (min)
T absolute temperature (K)
V volume of the reaction mixture (cm^3)
W catalyst weight ($g_{catalyst}$)

Indices:

max   maximum value
A, B, C   reaction components
I   inert solvent
1, 2   reaction steps
0   initial value

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