

# Kinetics of catalytic hydrogenation of 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,7-nonadien-4-yne-1,6-diol

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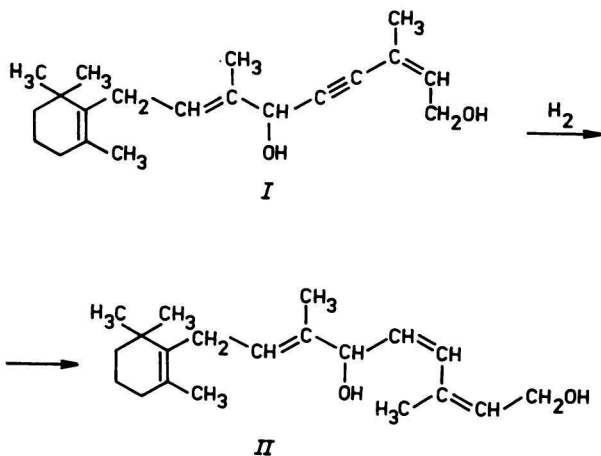
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Kinetics of hydrogenation of 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,7-nonadien-4-yne-1,6-diol in an isothermal batch suspension reactor was investigated. Examined was the influence of temperature (20–40 °C), hydrogen pressure (0.15–0.34 MPa) and mass ratio of the quinoline deactivated Lindlar catalyst (0.03–0.09) and the starting material on the velocity and the overall selectivity of hydrogenation.

3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,7-nonadien-4-yne-1,6-diol (*I*) is the starting material in the production of vitamin A according to the Isler procedure, in which compound *I* was catalytically hydrogenated to 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,4,7-nonatriene-1,6-diol (*II*) (Scheme 1). The unwanted by-products of this hydrogenation are the 4-*trans* isomer of compound *II* and further unspecified substances.



Scheme 1

As reported, compound *I* was hydrogenated to *II* in methanol over quinoline-deactivated palladium on charcoal in 97 % yield [1], in petroleum ether over the same catalyst deactivated by lead diacetate (Lindlar catalyst) in 84–86 % yield [2, 3] and over a modified catalyst in 89 % yield [4]. Optimization experiments afforded *II* in 88 % yield when using hexane with quinoline and lead diacetate-deactivated palladium on calcium carbonate [5]. Other hydrogenation conditions and solvents together with reaction velocities between  $1.9 \times 10^{-4} \text{ s}^{-1}$  and  $11.6 \times 10^{-4} \text{ s}^{-1}$  with activation energy  $42 \text{ kJ mol}^{-1}$  are presented in paper [6].

In this study we investigated the dependence of the reaction velocity and overall selectivity of hydrogenation on the mass ratio of the catalyst and compound *I*, on temperature and hydrogen pressure, data needed for modelling the catalytical process in an isothermal batch suspension autoclave. The experiments were carried out in petrol with the Lindlar catalyst in a 20–40 °C temperature range, because at a temperature below 20 °C compound *I* crystallized out and above 40 °C both compounds *I* and *II* are unstable.

## Experimental

3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,7-nonadien-4-yne-1,6-diol (*I*), crystalline, purity min. 95 % (Slovakofarma, Hlohovec), technical grade petrol 60/80 (Slovnaft, Bratislava); 10 % aqueous solution of palladium dichloride (Safina, Jesenice near Prague); precipitated calcium carbonate (99 %, Merck, Darmstadt); anhydrous sodium carbonate, pure (Lachema, Neratovice); 85 % formic acid (Lachema, Brno); lead diacetate, pure (Slovak Chemical Works, Hnúšťa); quinoline, synthetic pure (Lachema, Neratovice); electrolytic hydrogen in pressure cylinder (Technoplyn, Nováky); Lindlar catalyst prepared according to example 3, Ref. [3] without bismuth trinitrate (5 % palladium and 5 % lead over calcium carbonate of  $5.7 \text{ m}^2 \text{ g}^{-1}$  specific surface and 1.9 nm mean pore radius).

The equilibrium sorption data of nitrogen on the surface of the catalyst were measured at the temperature of liquid nitrogen with a gravimetric sorption apparatus Gravimat, model 4303 (Sartorius, FRG). The content of compounds *I* and *II* was estimated by the HPLC method on a Pye—Unicam Philips instrument employing a  $250 \times 0.4 \text{ mm}$  column packed with Separon SGX C (grain size  $18.7 \mu\text{m}$ ) and a  $0.025 \text{ cm}^3 \text{ s}^{-1}$  flow rate of the mobile phase (methanol—water,  $\phi_r = 4:1$ ) and a UV detector ( $\lambda = 220 \text{ nm}$ ).

## Hydrogenation procedure

Compound *I* (100 g;  $330 \text{ mmol}$ ), petrol ( $500 \text{ cm}^3$ ), catalyst (3.0–9.0 g), and quinoline ( $2.5 \text{ cm}^3$ ) were placed into a stainless steel  $2 \text{ dm}^3$  batch reactor equipped with an agitator (number of revolutions  $2100 \text{ min}^{-1}$ ) and a heating jacket. The hydrogen pressure in the

vessel was kept constant by pressing water into the graduated 5 dm<sup>3</sup>-cylinder filled with hydrogen and simultaneously serving for measuring its consumption. Conditions for hydrogenation experiments were standardized as follows: The reactor was first evacuated, flushed three times with hydrogen, the required temperature and pressure were set up and finally, the agitator was put into operation. During hydrogenation constant temperature was maintained ( $\pm 1^\circ\text{C}$ ). After the reaction had consumed approximately the calculated amount of hydrogen, the catalyst was filtered off and the solvent was distilled off under reduced pressure.

## Results and discussion

The overall selectivity of hydrogenation is understood as the ratio of masses of the required product *II* and consumed starting compound *I* [7]. Hydrogenation spontaneously stopped at the amount of hydrogen needed for saturation of the triple bond to a double one. The dependences of the degree of conversion of *I* on time at various mass ratios of catalyst and compound *I* are represented in Fig. 1, at various pressures in Fig. 2 and at various temperatures in Fig. 3.

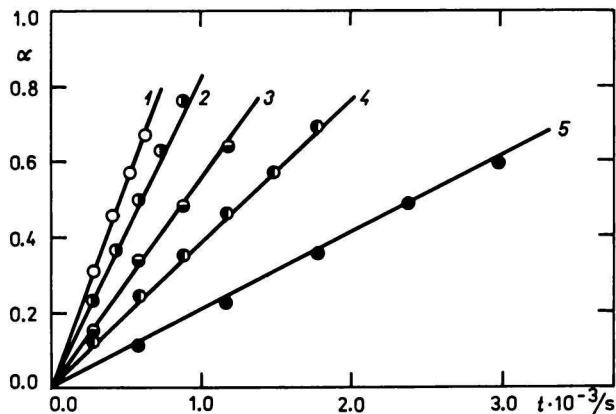


Fig. 1. Relationship between the degree of conversion of compound *I* and amount of the catalyst at 0.20 MPa and 30°C. 1. 9.0 g, 2. 7.5 g, 3. 6.0 g, 4. 4.5 g, 5. 3 g/100 g of *I*.

Relationship between the degree of conversion of *I* and time is linear which means that this catalytical hydrogenation is a reaction of zero order under the given reaction conditions. The measured data served for calculation of the rate constants (Table 1) for which, employing the Arrhenius equation, the value for activation energy  $E = 41.3 \pm 2.0 \text{ kJ mol}^{-1}$  was determined. In spite of the fact that the rate constants reported in [6] indicate the first-order reaction, the

apparent activation energy  $41.9 \text{ kJ mol}^{-1}$  is in a good agreement with that obtained in this study.

Investigation of the effect of temperature ( $20\text{--}40^\circ\text{C}$ ), pressure ( $0.15\text{--}0.34 \text{ MPa}$ ), and mass ratio ( $0.03\text{--}0.09$ ) of the quinoline-deactivated Lindlar catalyst on hydrogenation of *I* in an isothermal batch suspension autoclave showed that:

1. increase of the mass ratio of the catalyst and compound *I* remarkably enhanced the reaction velocity, whilst the overall selectivity decreased;

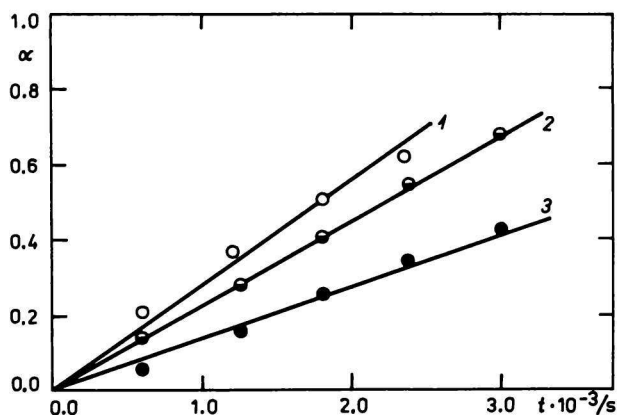


Fig. 2. Relationship between the degree of conversion of compound *I* and pressure of hydrogen applied at 3.0 g of the catalyst/100 g of *I* and  $30^\circ\text{C}$ . 1.  $0.34 \text{ MPa}$ ; 2.  $0.24 \text{ MPa}$ ; 3.  $0.15 \text{ MPa}$ .

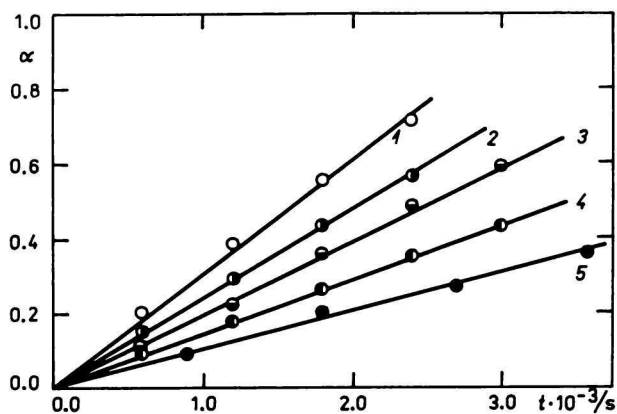


Fig. 3. Relationship between the degree of conversion of compound *I* and temperature applied at  $0.20 \text{ MPa}$  hydrogen pressure and 3.0 g of catalyst/100 g of *I*. 1.  $40^\circ\text{C}$ ; 2.  $35^\circ\text{C}$ ; 3.  $30^\circ\text{C}$ ; 4.  $25^\circ\text{C}$ ; 5.  $20^\circ\text{C}$ .

2. the stepwise increase of pressure from 0.15 to 0.34 MPa enhanced moderately the reaction velocity and the overall selectivity remained virtually constant;

3. increase of temperature from 20 to 40 °C resulted in a triple reaction velocity and a 10 % decrease of the overall selectivity;

4. this catalytical hydrogenation obeys the zero-order velocity equation and the rate constants vary within  $0.53 \times 10^{-4}$  and  $5.40 \times 10^{-4} \text{ kmol m}^{-3} \text{ s}^{-1}$ ; the overall selectivity was found to be 82.5–95.0 %.

Table 1

Calculated rate constant values and overall hydrogenation selectivities at various conditions

$\frac{m(\text{catalyst})}{m(I)}$	$\frac{p}{\text{MPa}}$	$\frac{\theta}{^\circ\text{C}}$	$\frac{k \cdot 10^4}{\text{kmol m}^{-3} \text{ s}^{-1}}$	Overall selectivity/%
0.030	0.20	30	$1.02 \pm 0.01$	88.0
0.045	0.20	30	$2.01 \pm 0.06$	86.4
0.060	0.20	30	$2.80 \pm 0.02$	85.2
0.075	0.20	30	$4.37 \pm 0.04$	84.6
0.090	0.20	30	$5.40 \pm 0.07$	82.5
0.030	0.34	30	$1.21 \pm 0.06$	88.0
0.030	0.24	30	$1.07 \pm 0.03$	86.9
0.030	0.15	30	$0.73 \pm 0.02$	88.1
0.030	0.20	20	$0.53 \pm 0.01$	95.0
0.030	0.20	25	$0.76 \pm 0.01$	92.1
0.030	0.20	35	$1.24 \pm 0.01$	86.9
0.030	0.20	40	$1.60 \pm 0.04$	85.9

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