

## EFFECT OF THE STRUCTURE OF UNSATURATED HYDROCARBONS AND ALCOHOLS ON THEIR REACTIVITY AND ADSORPTIVITY IN HYDROGENATION

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Competitive hydrogenations of unsaturated hydrocarbons and unsaturated alcohols using a palladium supported catalyst, were studied under atmospheric pressure at 25 °C. From the acquired data and from the hydrogenation of each individual substrate, kinetic and adsorption parameters were determined. It was found that the hydroxyl group position relative to the double bond has no significant effect on the reactivity of the studied unsaturated alcohols; however, it has a major effect on their adsorptivity. Reactivity and adsorptivity of unsaturated hydrocarbons depended on the double bond position in substrates.

**Key words:** Competitive hydrogenation; Palladium catalyst; Reactivity; Adsorptivity; Unsaturated hydrocarbons; Unsaturated alcohols; Selectivity; Heterogeneous catalysis.

Selectivity studies of catalytic hydrogenations still rank among contemporary tasks of heterogeneous catalysis. The obtained data gather valuable knowledge, significant not only for the general theory of hydrogenation reactions but also for industrial applications. Although there exists an immense amount of literature concerning selective hydrogenations of alkenes, only an insignificant percentage of the studies utilize the method of competitive hydrogenation reaction<sup>1-12</sup>. In this work, it was attempted to acquire competitive hydrogenation selectivities of the following systems: unsaturated hydrocarbon-unsaturated hydrocarbon, unsaturated hydrocarbon-unsaturated alcohol and unsaturated alcohol-unsaturated alcohol. These were formed with appropriate combinations of selected model substances (hept-1-ene, octa-1,7-diene, cyclohexene, prop-2-ene-1-ol, hex-1-ene-3-ol, hept-1-ene-4-ol, 2-methylbut-3-ene-2-ol) on a palladium catalyst in methanolic medium used as a solvent. The initial reaction rate values acquired during hydrogenations of individual substances were used to determine the relative adsorption coefficients of individual substrates. The obtained figures characterizing reactivity of substances and adsorptivity di-

vergences meant significant progress in the discussion about structural effects on these parameters.

## EXPERIMENTAL

### Chemicals

Commercial substrates, hept-1-ene, cyclohexene, 2-methylbut-3-ene-2-ol, hept-1-ene-4-ol (Koch-Light), octa-1,7-diene, hex-1-ene-3-ol (Aldrich), prop-2-ene-1-ol (Loba Feinchemie),  $\alpha$ -methylstyrene (Slovnaft) and cyclohexene (Koch-Light), were distilled before use. Methanol of analytical grade (Penta) and electrolytic hydrogen 4.0 (Linde Technoplyn) were used.

### Catalysts

The catalyst used, 3% Pd/C-Cherox 4100ch (Chemopetrol Ltd.), grain size  $<0.02$  mm, was characterized by the particle crystallite size (20.2 nm) and surface area ( $1\ 160\ \text{m}^2\ \text{g}_{\text{cat}}^{-1}$ ). The particle crystallite size was determined using an XRD Seifert with  $\text{CoK}\alpha$  and graphitic monochromator. The particle size was computed using a one-point method for the most intense line of the monitored material. Palladium catalyst showed a definite crystallite structure. Physical adsorption of nitrogen was measured using a Pulse Chemisorb 2700 system (Micromeritics); the total surface area ( $S_{\text{BET}}$ ) was evaluated from the BET region. The measurement of surface of the activated-carbon supported catalyst was subject to error, caused by the instrumentation used which, due to its great extent, did not enable an exact determination. The error reached up to 10% of the determined value.

### Apparatus and Kinetic Measurements

Kinetic measurements were carried out in a semibatch stirred reactor at  $25\ ^\circ\text{C}$  under hydrogen pressure of 101.3 kPa in methanol. A detailed description of the equipment is given elsewhere<sup>13</sup>. All the measurements were carried out in the kinetic region. The external diffusion effect was eliminated by using a sufficiently effective stirring and the internal diffusion effect by using a fine powder catalyst. The reaction course was monitored by measuring the time dependence of hydrogen consumption and time changes in molar concentrations obtained by chromatographic analysis (GLC). In hydrogenations, 2 mmol of substrate was used, 1 mmol of each substrate in 15 ml of methanol in competitive hydrogenations. The catalyst amount ranged between 10.0–15.0 mg depending on the substrate used.

### Analytical Method

Samples withdrawn at appropriately selected time intervals were analyzed using a gas chromatograph Shimadzu GC-17A with flame-ionization detector (FID) and capillary column J&W Scientific DB-5 (length 30 m, inner diameter 0.32 mm, thickness of stationary phase  $1.0\ \mu\text{m}$ ) with temperature programs between 328–423 K and overpressure of carrier gas ( $\text{N}_2$ ) 80 kPa. Gas chromatograph Finnigan 9001 with FID detector and capillary column Alltech EC-5 (length 30 m, inner diameter 0.32 mm, thickness of stationary phase  $0.25\ \mu\text{m}$ ) with temperature programs between 333–453 K and overpressure of carrier gas ( $\text{N}_2$ ) 80 kPa was used as well. The substance contents in the reaction mixture were determined using the internal standard method. The internal standard was n-decane (Aldrich).

## RESULTS AND DISCUSSION

*Hydrogenation of Individual Substrates*

The measured time-concentration dependences  $c = f(t)$  for individual hydrogenations of chosen substrates were used to determine the initial reaction rate values. Subsequently, these values were employed for calculation of relative adsorption coefficients. Most of the reactions were of zeroth order with respect to substrate concentrations, even at high conversions.

The hydrogenations with a palladium catalyst were accompanied by double-bond isomerization<sup>14,15</sup> (the presence of hept-2-ene in hept-1-ene hydrogenation and a variety of octene isomers in octa-1,7-diene hydrogenation were detected using gas chromatography), which resulted in aldehyde and ketone formation from the unsaturated alcohols<sup>16</sup> (propanal from prop-2-ene-1-ol, hexan-3-one from hex-1-ene-3-ol and heptan-4-one from hept-1-ene-4-ol). In prop-2-ene-1-ol hydrogenation, though to a limited extent, the hydroxyl group hydrogenolysis also occurred. Nevertheless, the concentration of these side products did not exceed few per cent and hydrogenolysis had no influence on the reaction rates.

The summary of the initial reaction rates  $r_0$  for individual substrate, is provided in Table I. It is implied that the highest initial reaction rate was observed in the hept-1-ene hydrogenation, *i.e.* with a compound having only one terminal double bond. On the contrary, hydrogenation of a model compound with a nonterminal double bond, cyclohexene, as it occurs in the cyclic chain, proceeded with the lowest reaction rate. A specula-

TABLE I  
Initial hydrogenation rates of substrates on Pd/C

Substrate	$r_0$ , mol min <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup>
Hept-1-ene	0.29 ± 0.04
Octa-1,7-diene	0.13 ± 0.02
Cyclohexene	0.023 ± 0.002
Prop-2-ene-1-ol	0.068 ± 0.009
Hex-1-ene-3-ol	0.077 ± 0.001
Hept-1-ene-4-ol	0.077 ± 0.008
2-Methylbut-3-ene-2-ol	0.073 ± 0.005

tive explanation of the differences in the initial reaction rate of octa-1,7-diene and hept-1-ene could be based on the mechanism of octa-1,7-diene adsorption. This can be bonded on the catalyst surface with its two double bonds, and the hydrocarbon chain between them may thus hinder access to the vacant catalytic centres, needed for adsorption of another molecule of octa-1,7-diene, leading to a general decrease in the reaction rate. Table I makes it also clear that the structure modification had no significant effect on the initial reaction rate of studied alcohols.

### *Competitive Hydrogenations in Binary Systems*

A relatively simple relation for selectivity, defined using the ratio of reactivities of both substances, can be established if the kinetics of the substances involved in a competitive reaction can be expressed with an equation of the same form. If the rate-determining step is a surface reaction and the reaction is carried out far from equilibrium, in the simplest case with an assumption of ideal behavior, it is possible to write for the hydrogenation of A and B substrates:

$$r_A = \frac{k_{AH} K_A c_A}{1 + K_A c_A + K_B c_B + K_H c_H} = -\frac{dc_A}{dt} \frac{V}{w}, \quad (1)$$

$$r_B = \frac{k_{BH} K_B c_B}{1 + K_B c_B + K_A c_A + K_H c_H} = -\frac{dc_B}{dt} \frac{V}{w}. \quad (2)$$

The hydrogen concentration and its adsorption constant are included in the kinetic constant  $k_{AH}$ . From Eqs (1) and (2), it is possible to derive a relation for the selectivity of competitive hydrogenation commonly known as the Rader-Smith equation<sup>17</sup>:

$$\frac{\log(c_A / c_{A0})}{\log(c_B / c_{B0})} = \frac{k_{AH} K_A}{k_{BH} K_B} = S_{AB}. \quad (3)$$

In ideal case, the dependence  $\log (c_A/c_{A0})$  on  $\log (c_B/c_{B0})$  is a straight line characterized by the slope  $S_{AB}$ . The measured data fulfilled the linear characteristic of this equation very well, which is apparent from the values of correlation coefficients ( $f$ ) ranging from 0.90 to 1.00. Since instantaneous concentrations of initial components were substituted for  $c_A$  and  $c_B$ , such defined selectivity also included isomerizations of the substrate. Table II shows  $S_{AB}$  selectivity values acquired using this procedure. Relative adsorption coefficients  $K_A/K_B$ , shown also in Table II, were computed using the acquired  $S_{AB}$  values and initial reaction rates  $r_0$  of hydrogenations of individual substrate, which were in the above equation substituted for reaction rate coefficients  $k_{AH}$  and  $k_{BH}$ .

Table II documents that out of all the tested unsaturated compounds, octa-1,7-diene was the most sorbed on the palladium catalyst, and prop-2-ene-1-ol being the second. The factual behavior of octa-1,7-diene can be explained by dual-site adsorption on the catalyst surface, due to its two terminal double bonds. The comparable selectivity of prop-2-ene-1-ol is apparently caused by a positive effect of hydroxyl group bonded to an  $\alpha$ -carbon of the terminal double bond.

The effect of the remaining hydrocarbon chain (the propyl group) in hex-1-ene-3-ol is disputable. This substrate is, by its hydroxyl group position relative to the terminal double bond, comparable with prop-2-ene-1-ol. An equal adsorptivity in systems with hept-1-ene was in accordance with this fact. On the other hand, hex-1-ene-3-ol was sorbed in other competitive hydrogenations less than structurally similar prop-2-ene-1-ol, which became apparent from the competitive hydrogenation of these two substrates.

Compared with the above discussed alcohols, the further shift of the hydroxyl group by two carbons away from the terminal double bond in hept-1-ene-4-ol along the unsaturated chain, a decrease in adsorptive ability of this substance was observed. The relative adsorption coefficient of the hept-1-ene-hept-1-ene-4-ol system was comparable, which proves that a more distant hydroxyl group has no significant effect on the adsorption of terminal double bond in this system. Thus the actual hydroxyl group does not play any significant role in the adsorption mechanism. For the other systems, it is not possible to unequivocally state, which of the provided substrates (hept-1-ene or hept-1-ene-4-ol) exhibited a higher adsorptivity because the relative adsorption coefficients, to a certain extent, depended also on the structure of the reference substrate.

The next in the order of decreasing adsorptivity on the palladium catalyst, is 2-methylbut-3-ene-2-ol. Adsorption of this substrate was preferred

only in the system with cyclohexene, which exhibited absolutely the worst adsorption on the palladium catalyst, relative to all the mentioned substances in all the model systems. The cause of the low adsorption ability of 2-methylbut-3-ene-2-ol can be the presence of methyl group on the carbon next to the terminal double bond or the actual high degree of substitution on this carbon with bonded hydroxyl group, or a combination of both these factors. The presence of the hydroxyl group next to a double bond, as

TABLE II  
Competitive hydrogenations in binary systems

Substrate A	Substrate B	$S_{AB}$	$f$	$r_{A0}/r_{B0}$	$K_A/K_B$
Hept-1-ene	Cyclohexene	$59 \pm 4$	0.9593	$12.6 \pm 0.7$	$5 \pm 1$
Octa-1,7-diene	Cyclohexene	$31 \pm 3$	0.9090	$5.6 \pm 0.9$	$6 \pm 1$
Octa-1,7-diene	Hept-1-ene	$1.7 \pm 0.1$	0.9673	$0.45 \pm 0.01$	$3.7 \pm 0.3$
Prop-2-ene-1-ol	Hept-1-ene	$0.93 \pm 0.05$	0.9710	$0.24 \pm 0.01$	$3.9 \pm 0.4$
Hex-1-ene-3-ol	Hept-1-ene	$1.05 \pm 0.01$	0.9973	$0.27 \pm 0.03$	$4.0 \pm 0.5$
Hept-1-ene-4-ol	Hept-1-ene	$0.275 \pm 0.006$	0.9942	$0.27 \pm 0.01$	$1.02 \pm 0.06$
2-Methylbut-3-ene-2-ol	Hept-1-ene	$0.19 \pm 0.01$	0.9593	$0.26 \pm 0.02$	$0.74 \pm 0.09$
Prop-2-ene-1-ol	Cyclohexene	$142 \pm 8$	0.9883	$3.0 \pm 0.2$	$48 \pm 6$
Hex-1-ene-3-ol	Cyclohexene	$27.8 \pm 0.8$	0.9876	$3.4 \pm 0.3$	$8.3 \pm 0.9$
Hept-1-ene-4-ol	Cyclohexene	$23.3 \pm 0.5$	0.9862	$3.3 \pm 0.1$	$7.1 \pm 0.4$
2-Methylbut-3-ene-2-ol	Cyclohexene	$12.2 \pm 0.3$	0.9905	$3.2 \pm 0.1$	$3.8 \pm 0.2$
Prop-2-ene-1-ol	Octa-1,7-diene	$0.44 \pm 0.01$	0.9971	$0.53 \pm 0.02$	$0.83 \pm 0.05$
Hept-1-ene-4-ol	Octa-1,7-diene	$0.084 \pm 0.001$	0.9964	$0.60 \pm 0.03$	$0.14 \pm 0.01$
2-Methylbut-3-ene-2-ol	Octa-1,7-diene	$0.40 \pm 0.01$	0.9709	$0.57 \pm 0.05$	$0.07 \pm 0.01$
Prop-2-ene-1-ol	Hex-1-ene-3-ol	$3.50 \pm 0.04$	0.9985	$0.89 \pm 0.09$	$4.0 \pm 0.5$
Prop-2-ene-1-ol	Hept-1-ene-4-ol	$5.9 \pm 0.1$	0.9925	$0.89 \pm 0.03$	$6.7 \pm 0.4$
Prop-2-ene-1-ol	2-Methylbut-3-ene-2-ol	$13.9 \pm 0.5$	0.9804	$0.93 \pm 0.06$	$15 \pm 2$
Hex-1-ene-3-ol	Hept-1-ene-4-ol	$1.82 \pm 0.09$	0.9269	$1.01 \pm 0.09$	$1.8 \pm 0.2$
Hex-1-ene-3-ol	2-Methylbut-3-ene-2-ol	$2.9 \pm 0.1$	0.9735	$1.06 \pm 0.06$	$2.8 \pm 0.3$
Hept-1-ene-4-ol	2-Methylbut-3-ene-2-ol	$1.96 \pm 0.02$	0.9978	$1.05 \pm 0.04$	$1.9 \pm 0.1$

it was discussed in the case of prop-2-ene-1-ol, affects the adsorptivity positively. The presence of a hydrocarbon chain, which is in the case of 2-methylbut-3-ene-2-ol represented by one methyl group, rather prevents other adsorption on this carbon, as it was explained with the hex-1-ene-3-ol. In the case of 2-methylbut-3-ene-2-ol, the carbon next to the terminal double bond is substituted with one more methyl group.

In conclusion: using catalytic hydrogenation of  $C_3$ – $C_7$  unsaturated alcohols with Pd/C catalyst, it was found, that the hydroxyl group position relative to the double bond has no significant effect on the reactivity of unsaturated alcohols. However, differences in reactivity of unsaturated hydrocarbons were observed. Furthermore, it was found that adsorptivity of unsaturated alcohols is affected by several factors. It decreases with the degree of substitution of double bond, with increasing distance of a hydroxyl group from the double bond, and with increasing degree of substitution of the carbon, bearing the hydroxyl group. The adsorptivity of unsaturated hydrocarbons decreased with increasing degree of substitution of a double bond.

## SYMBOLS

A	substrate (to be hydrogenated)
B	substrate (to be hydrogenated)
$c_A$	concentration of substance A, mol dm <sup>-3</sup>
$c_{A0}$	initial concentration of substrate A, mol dm <sup>-3</sup>
$f$	correlation coefficient
$k_A$	rate constant of hydrogenation of substrate A
$K_A$	adsorption coefficient of substrate A
$K_A/K_B$	relative adsorption coefficient
$r_A$	rate of hydrogenation of substrate A, mol min <sup>-1</sup> g <sup>-1</sup> <sub>cat</sub>
$S_{AB}$	selectivity of competitive hydrogenation of substrates A and B
$S_{BET}$	total surface area, m <sup>2</sup> g <sup>-1</sup> <sub>cat</sub>
$t$	time, min
$V$	volume of reaction mixture, dm <sup>3</sup>
$w$	amount of catalyst, g

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