

## EFFECT OF SOLVENTS ON THE CATALYTIC HYDROGENATION OF 1,5-HEXADIEN-3-OL

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Catalytic hydrogenation of 1,5-hexadien-3-ol on 5% Pt on silica gel as catalyst in seven solvents under ordinary conditions was examined. 3-Hexanol is obtained *via* 1-hexen-3-ol and 1-hexen-4-ol as intermediates. Rate constants of the particular steps were measured and the relative adsorption coefficient values determined from integrated kinetic equations. The influence of the solvent on the rate constant and adsorption constant was examined.

The present paper is a continuation of the earlier investigations<sup>1-6</sup> on the influence of solvents on the course of catalytic hydrogenations. As inferred from hydrogenations of some unsaturated alcohols<sup>5</sup>, the reaction rate is affected by the position of both the double bond and the hydroxylic function. The reaction rate decreases with the substitution degree on the double bond and on the carbon atom to which the hydroxylic function is attached. Hydrogenation of the alcohol with the hydroxylic function at the  $\alpha$ -position with respect to the double bond was slower than that of the alcohol with the OH group at the  $\beta$ -position. Sensitivity of reaction rates towards solvents (expressed<sup>1</sup> by the parameter  $\lambda'$ ) decreased in the order secondary alcohol with the OH group at the  $\alpha$ -position with respect to the monosubstituted double bond, secondary alcohol with the OH group at the  $\beta$ -position with respect to the monosubstituted double bond, primary alcohol with a disubstituted double bond, and primary alcohol with a monosubstituted double bond. It has been observed<sup>5</sup> that also the adsorptivity of unsaturated alcohols on platinum catalyst is affected by position of both the double bond and the hydroxylic group. Thus, the adsorptivity decreases with the number of substituents on the double bond, distance of the OH group from the double bond, and number of substituents on the carbon atom bearing the OH group.

In the present work, the course of hydrogenation was examined with the use of 1,5-hexadien-3-ol containing double bonds at positions  $\alpha$  and  $\beta$  with respect to the OH group. This alkadienol along with the intermediate alkenols make possible to examine the selectivity of the hydrogenation of the double bonds at positions  $\alpha$  and  $\beta$  with respect to the OH group in one molecule or two various molecules.

### EXPERIMENTAL

*Materials.* The 5% Pt on silica gel catalyst was prepared similarly to ref.<sup>1</sup> A fraction of the particle size below 0.063 mm was used. Cyclohexane, diethyl ether, toluene, methanol, benzene, ethyl acetate, and 1,4-dioxane were used as solvents. Their purification was similar to ref.<sup>1</sup> All

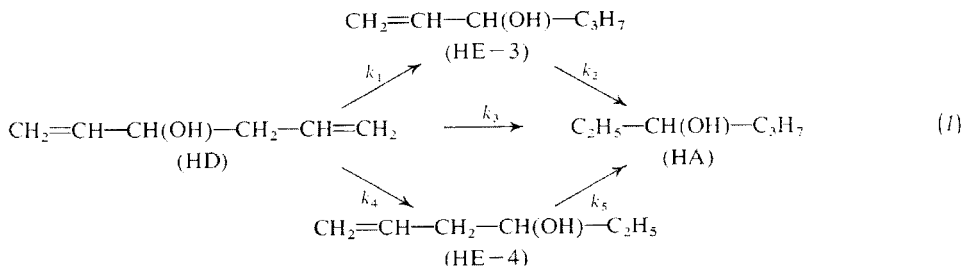
solvents were chromatographically homogeneous and were redistilled before use. The electrolytical hydrogen (Technoplyn, Pardubice, Czechoslovakia) was used directly. 1,5-Hexadien-3-ol (b.p. 133–134°C), 1-hexen-3-ol (b.p. 134°C), and 1-hexen-4-ol (b.p. 129–132°C) were prepared by the Grignard reaction<sup>7,8</sup>. 1,5-Hexadien-3-ol was obtained from allylmagnesium bromide and acrolein, 1-hexen-3-ol from propylmagnesium bromide and acrolein, and 1-hexen-4-ol from allylmagnesium bromide and 1-propanal. The alcohols were rectified and the chromatographically homogeneous distillate fractions used in hydrogenations.

*Apparatus and measurements.* The apparatus and methods have been described earlier in refs<sup>1–3</sup>. Hydrogenations were performed in a stirred reactor at 20°C under the atmospheric pressure of hydrogen with the use of 2 ml of the substrate and 25 ml of the particular solvent. The amount of the catalyst varied from 0.1 g to 0.3 g according to absolute rates of the hydrogenation in the particular solvent. The time dependence of the hydrogen uptake was checked by means of a burette and when the uptake was 50 ml of hydrogen, samples of the hydrogenation mixture (0.1 ml each) were withdrawn for the chromatographic analysis.

Gas chromatography. Analyses were carried out on the CHROM-2 gas chromatograph with flame-ionisation detection at 90°C. The glass column (length, 2.8 m; internal diameter, 2.5 mm) was packed with 20% poly(ethylene glycol) 600 on Chezasorb (particle size, 0.16–0.20 mm). Relative elution times: 1.00, 3-hexanol; 1.08, 1-hexen-4-ol; 1.30, 1-hexen-3-ol; and 1.58, 1,5-hexadien-3-ol.

## RESULTS AND DISCUSSION

Kinetic measurements were performed under conditions not affecting the reaction rate by mass transport<sup>1,3</sup>. Hydrogenation of 1,5-hexadien-3-ol was observed to proceed according to the following Scheme 1:



The formation of 3-hexanol (HA) according to this reaction Scheme (1) was accompanied by production of hexane by side reactions, probably dehydration of alcohols on the acidic carrier (SiO<sub>2</sub>) of the catalyst and the subsequent hydrogenation of the resulting unsaturated hydrocarbons. The amount of hexane (corresponding to 1–3% conversion of 1,5-hexadien-3-ol) was not taken into account in evaluations of the final reaction mixtures with respect to the ratio of components.

The reaction rate of the hydrogenation of 1,5-hexadien-3-ol was observed to decrease particularly in the early 10 minutes. This decrease is especially perceptible in nonpolar solvents (toluene, benzene) and is obviously due to the initially formed

water and its dissolution in the reaction medium. After a certain period of time, the decrease of the reaction rate was much slower and almost equal in all solvents. A further dehydration of 1,5-hexadien-3-ol is apparently strongly slowed down since the active centres are occupied by the primarily formed water. The achievement of the steady state of the catalyst activity was so rapid that the time dependence of the alcohol concentration was not affected (Fig. 1); despite a moderate decrease of the reaction rate in the initial ten minutes, the reaction order with respect to the concentration of 1,5-hexadien-3-ol was zero in all solvents up to the 70% conversion of 1,5-hexadien-3-ol.

As determined in separate hydrogenations of 1-hexen-3-ol and 1-hexen-4-ol with the use of the stated set of concentrations, the reaction is also of the pseudozero order with respect to the initial and instantaneous concentration of the particular alcohol and the reaction rate is in this case equal to the reaction constant. The values of initial reaction rates (rate constants) were obtained as slopes of tangents in time  $t = 0$  to the time dependence of the particular alcohol concentrations. Constants  $k_2$  and  $k_5$  were obtained in separate hydrogenations of 1-hexenols and constants  $k_1$ ,  $k_3$ , and  $k_4$  were inferred from initial rates of the formation of 1-hexen-3-ol, 3-hexanol, and 1-hexen-4-ol from 1,5-hexadien-3-ol. The observed reaction constants are shown in Table I (indices are identical with those in Scheme 1).

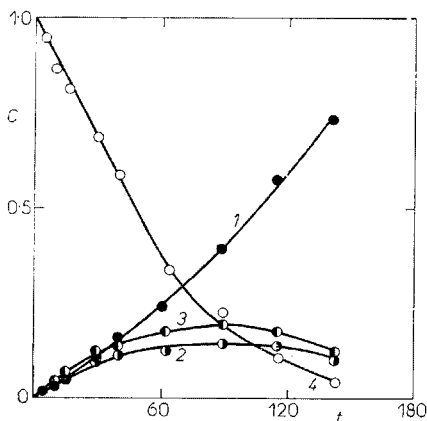


FIG. 1

Time Dependence of Concentrations of the Particular Components in the Hydrogenation of 1,5-Hexadien-3-ol in Benzene

1 3-Hexanol, 2 1-hexen-4-ol, 3 1-hexen-3-ol, 4 1,5-hexadien-3-ol.

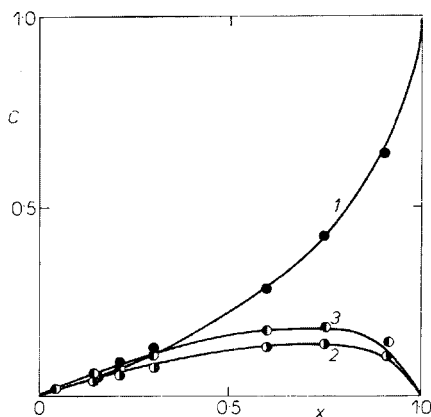


FIG. 2

Calculated Concentration Dependence of Intermediates and of the Product on the Conversion of 1,5-Hexadien-3-ol (experimental values are designated by dots)

1 3-Hexanol, 2 1-hexen-4-ol, 3 1-hexen-3-ol.

The rate constants were corrected<sup>1-3</sup> to the hydrogen pressure of 98 kPa (760 Torr) and to the solvent vapour pressure under the assumption of a first order reaction with respect to the partial pressure of hydrogen. The adsorption constants of the particular components were estimated with the use of the simplest version of the Langmuir-Hinshelwood type equation for the slowest step of the reaction on the catalyst surface taking into account adsorption on a single active centre only. Such an approach can be regarded as formal since more likely the adsorption of the dienol occurs on two active centres. Another simplification consists in the assumption that the adsorption constants of 1,5-hexadien-3-ol are the same in all reactions taking place on the catalyst. Nevertheless, in view of the present examination of relations between the kinetic and adsorption constants of the particular substrates in various solvents, such an approach appears adequate.

In order to eliminate the influence of decreasing catalyst activity, the time coordinate was replaced by the concentration coordinate (concentrations of the intermediary 1-hexen-3-ol and 1-hexen-4-ol, and the final 3-hexanol were plotted versus the concentration of the starting 1,5-hexadien-3-ol). The relative data obtained by this modification are satisfactory<sup>9</sup>.

By elimination of time from the starting kinetic equations, relations (1), (2), and (3) are obtained:

$$-\frac{dC_{\text{HE-3}}}{dC_{\text{HD}}} = \frac{k_1 K_{\text{HD}} C_{\text{HD}} - k_2 K_{\text{HE-3}} C_{\text{HE-3}}}{(k_1 + k_3 + k_4) K_{\text{HD}} C_{\text{HD}}} \quad (1)$$

$$-\frac{dC_{\text{HE-4}}}{dC_{\text{HD}}} = \frac{k_4 K_{\text{HD}} C_{\text{HD}} - k_5 K_{\text{HE-4}} C_{\text{HE-4}}}{(k_1 + k_3 + k_4) K_{\text{HD}} C_{\text{HD}}} \quad (2)$$

TABLE I  
Rate Constants

No	Solvent <sup>a</sup>	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
2	cyclohexane	10.2	51.5	7.2	7.2	38.2
4	diethyl ether	10.1	94.6	8.2	8.2	100.0
10	toluene	13.6	56.6	13.0	13.0	59.1
11	methanol	2.6	67.3	1.8	2.6	60.5
12	benzene	13.7	33.2	9.6	9.6	28.8
13	ethyl acetate	8.5	77.1	6.8	6.1	58.0
15	1,4-dioxane	2.4	19.2	1.8	1.8	16.6

<sup>a</sup> The numbering of solvents corresponds to that in refs<sup>1-5</sup>.

$$\frac{dC_{HA}}{dC_{HD}} = \frac{k_2 K_{HE-3} C_{HE-3} + k_3 K_{HD} C_{HD} + k_5 K_{HE-4} C_{HE-4}}{(k_1 + k_3 + k_4) K_{HD} C_{HD}} \quad (3)$$

Ratios  $K_{HE-3}/K_{HD}$  and  $K_{HE-4}/K_{HD}$ , *i.e.*, relative adsorption constants of 1-hexen-3-ol and 1-hexen-4-ol referred to 1,5-hexadien-3-ol were thus required. The numerical integration of equations (1) to (3) was performed after introduction of rate constant values by the method of Runge, Kutta and Merson on the Hewlett-Packard 2016B computer. From concentration coordinates at maxima of intermediates, the relative adsorption constants  $K_{HE-3}/K_{HD}$  and  $K_{HE-4}/K_{HD}$  were estimated and concentration curves of intermediates and the final product of the hydrogenation of 1,5-hexadien-3-ol were calculated with the use of equations (1) to (3). The calculated curves were graphically compared with experimental curves. On the basis of this comparison, the relative adsorption constant values were corrected and the calculation repeated with the use of these corrected values. The calculation was finished when a good agreement between the calculated and experimental curves was obtained (Fig. 2).

Fig. 2 shows dependence of the concentration of intermediates and the product of the hydrogenation of 1,5-hexadien-3-ol in dioxane on the degree of conversion of the starting substance, as obtained after introduction of constants by the numerical integration of equations (1) to (3); dots designate the experimental values. A similar course was observed and calculated with the use of some other solvents.

From concentrations of intermediates at maximum, the selectivity of the investigated reaction system can be defined. The selectivity between 1,5-hexadien-3-ol and 1-hexen-3-ol or 1-hexen-4-ol is given by the following equations

$$S_{HD,HE-3} = C_{HE-3}^{\max}/C_{HD1} = k_1 K_{HD}/k_2 K_{HE-3}, \quad (4)$$

$$S_{HD,HE-4} = C_{HE-4}^{\max}/C_{HD2} = k_4 K_{HD}/k_5 K_{HE-4}. \quad (5)$$

Numbers 1 and 2 at the concentration of 1,5-hexadien-3-ol designate that different concentrations are involved corresponding to the concentration maximum of the particular intermediate. From equations (4) and (5), the selectivity between intermediates may be obtained (6):

$$S_{HE-3,HE-4} = k_2 k_4 K_{HE-3}/k_1 k_5 K_{HE-4}. \quad (6)$$

The selectivity  $S_{HE-3,HE-4}$  expresses not only the uptake of the particular intermediates but also includes rate constants of their formation. The selectivity of the competitive hydrogenation of 1-hexen-3-ol and 1-hexen-4-ol is given by equation (7):

$$S_{HE-3,HE-4}^0 = k_2 K_{HE-3}/k_5 K_{HE-4}. \quad (7)$$

Table II shows values of relative adsorption constants and selectivities. The  $S_{HE-3,HE-4}$  selectivity values in column 1 were obtained from maxima of concentra-

TABLE II  
Relative Adsorption Constants and Selectivities

No	Solvent	$\frac{K_{HE-3}}{K_{HD}}$	$\frac{K_{HE-4}}{K_{HD}}$	$\frac{K_{HE-3}}{K_{HE-4}}$	$S_{HE-3,HE-4}$		$S_{HE-3,HE-4}^0$	
					1	2	1	2
2	cyclohexane	0.32	0.28	1.14	1.02	1.09	1.19	1.54
4	diethyl ether	0.24	0.19	1.26	1.00	0.97	1.08	1.19
10	toluene	0.35	0.40	0.87	0.75	0.79	0.94	0.83
11	methanol	0.06	0.07	0.85	0.78	0.95	0.94	0.95
12	benzene	0.60	0.60	1.00	0.91	0.81	1.10	1.15
13	ethyl acetate	0.19	0.21	0.90	0.94	0.86	1.08	1.20
15	1,4-dioxane	0.20	0.21	0.95	1.06	0.83	1.22	1.10

tion coordinates, those in column 2 by calculation from constants according to equation (6). The  $S_{HE-3,HE-4}^0$  selectivity data in column 1 were obtained from competitive hydrogenations of the two intermediates, those in column 2 by calculation from constants according to equation (7). A satisfactory agreement of values in columns 1 and 2 may be observed. The results of the kinetic analysis of competitive and separate reactions of 1-hexen-3-ol and 1-hexen-4-ol as well as of the overall conversion of 1,5-hexadien-3-ol may thus be regarded as consistent.

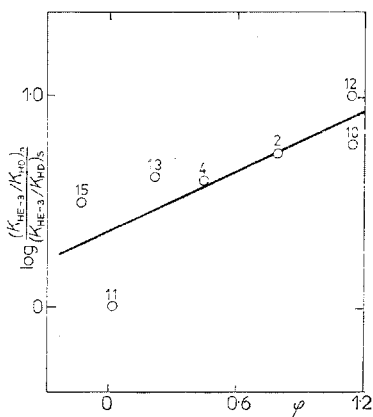


FIG. 3  
Dependence of the Logarithm of 1-Hexen-3-ol Adsorption Constant Ratios Referred to 1,5-Hexadien-3-ol in the Solvent  $n$  and in a Standard Solvent on the Parameter  $\phi$

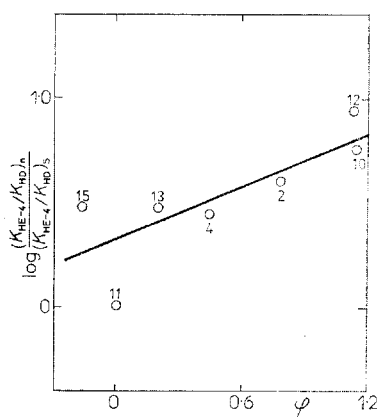


FIG. 4  
Dependence of the Logarithm of 1-Hexen-4-ol Adsorption Constant Ratios Referred to 1,5-Hexadien-3-ol in the Solvent  $n$  and in a Standard Solvent on the Parameter  $\phi$

The data obtained in hydrogenations of 1-hexen-3-ol and 1-hexen-4-ol are not at variance with the earlier<sup>5</sup> observed structural effects on the reactivity and adsorptivity of unsaturated alcohols. In most solvents, the hydrogenation of 1-hexen-3-ol was faster but the differences in reaction rates and adsorptivities were small. Both unsaturated alcohols exhibit a monosubstituted double bond and the carbon atom to which the OH group is attached, is in both cases substituted by one alkenyl group and one alkyl group.

In the hydrogenation of 1,5-hexadien-3-ol, the  $\beta$ -double bond (with respect to the OH group) was hydrogenated more fastly ( $k_1 > k_4$ ) in all solvents examined, but the differences were insignificant again. The influence of solvents on the selectivity of the hydrogenation of 1,5-hexadien-3-ol was small.

The most marked solvent effect has been observed in the case of rate constants of reactions resulting in disappearance of 1,5-hexadien-3-ol and in the case of relative adsorption coefficient  $K_{HE-3}/K_{HD}$  and  $K_{HE-4}/K_{HD}$  values. Thus, the lowest values of rate constants  $k_1$ ,  $k_3$ , and  $k_4$  have been observed in solvents (methanol, ethyl acetate, 1,4-dioxane) favouring the adsorption of 1,5-hexadien-3-ol. This interesting compensation of the kinetic and adsorption therm has also been encountered in some other cases<sup>5,10</sup>.

As shown by correlation of rate constants with the  $\tau'$  parameter (for the definition see an earlier paper<sup>1</sup>), the value of the correlation coefficient is low. This result does not surprise since 1,5-hexadien-3-ol is quite another substrate than cyclohexene which was used to define the parameter  $\tau'$ .

Figs 3 and 4 show the dependence of the logarithm of relative adsorption constants of 1-hexen-3-ol and 1-hexen-4-ol with respect to 1,5-hexadien-3-ol on the  $\varphi$  parameter. The correlation coefficient values ( $r_{xy} = 0.774$  and  $0.800$ , resp.) were in both cases higher than the critical value ( $r_{xy}$  krit. =  $0.755$  for the 95% significance level). The highest deviation from the calculated regression curves is shown by dots No 11 (methanol). Analogously to ref.<sup>5</sup>, linear regression gave straight lines obeying the equation (8)

$$\log (K_{i,j})_n / (K_{i,j})_s = \gamma\varphi + q, \quad (8)$$

*i.e.*, a relation with an absolute member, the physical meaning of which is obscure. As confirmed by correlation of relative adsorption constants with  $\varphi$ , the validity of the  $\varphi$  parameter is more general than that of  $\tau'$ .

#### LIST OF SYMBOLS

C	dimensionless concentration = instantaneous concentration of the particular substance referred to the initial concentration of 1,5-hexadien-3-ol
HA	3-hexanol
HD	1,5-hexadien-3-ol

HE-3	1-hexen-3-ol
HE-4	1-hexen-4-ol
$i, j$	general designation of the substrate
$K_{rel}$	relative adsorption constant
$k$	rate constant ( $\text{ml H}_2/\text{min g}_{\text{kat}}$ )
$n$	index designating the solvent
$q$	absolute member in the equation (8)
$r_{xy}$	correlation coefficient
$s$	index designating the solvent taken as the basis of the correlation (methanol)
$S$	selectivity
$t$	time (min)
$x$	conversion
$\varphi$	parameter characterising <sup>3</sup> the influence of the solvent on the relative adsorptivity of substrates
$\tau'$	parameter characterising <sup>3</sup> the influence of the solvent on the rate constant of the hydrogenation
$\gamma$	parameter of equation (9) characterising the sensitivity of the change of the relative adsorptivity with respect to the change of the solvent

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