KINETICS OF HYDROGENATION OF ALKYNES AND DIENES ON PALLADIUM CATALYST

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Alkynic and dienic substrates (C_6—C_{10}) in hexane and methanol were hydrogenated over a catalyst of 3% Pd on activated carbon at 20°C and atmospheric pressure. The initial reaction rates were measured for the individual substrates; the hydrogenation rates of the olefinic substances formed were also determined if the hydrogenation was selective. The selectivities in competitive hydrogenations of substrate pairs were established and the relative adsorption coefficients of the substrates were calculated from them. The effect of the substrate structure and the solvent effect on the hydrogenation rate and relative adsorptivity are discussed for the alkynic and dienic substances studied.

Owing to their high selectivity, palladium catalysts are conventionally used for the hydrogenation of alkynes and dienes. This high selectivity is due to the relatively high adsorptivity of these substrates as compared to olefins, owing to which the latter are usually hydrogenated only after all the starting substance has been taken up[1]. Under otherwise identical conditions, the selectivity depends on the structure of the substrate hydrogenated.

Few studies have been devoted to the problem of the effect of structure of alkynic or dienic substrates on the kinetics of their hydrogenation, and conclusions concerning limited structure series only could be drawn from them. A review of these studies has been presented by Červený and Růžička[2].

Making possible a comparison of the results of the present work with those by other authors, the papers by Sokolskaya[3−5] are of interest. The author found[3] that the hydrogenation rates on the 5% Pd/BaSO$_4$ catalyst decrease in order 3-heptyne > 2-heptyne > 1-pentyne > 1-heptyne, and she suggests that monosubstituted acetylenic hydrocarbons are hydrogenated in the absence of adsorbed hydrogen on the surface of the catalyst whereas disubstituted and trisubstituted hydrocarbons are hydrogenated in its presence. For substances of similar structure, the rate usually decreases with increasing molecular weight of the alkyne. In her next work[4], the author subjected a series of eight alkynes to hydrogenation on Pt black and Pd/BaSO$_4$ catalysts in 0·1M-KOH and 0·1M-HCl solutions. The hydrogenation rate decreased with the triple bond shifting towards the centre of the hydrocarbon chain. In hydro-

genations of alkyl ethynyl carbinols over Pd/BaSO$_4$ and Pd/CaCO$_3$ catalysts in 96% ethanol, the hydrogenation rate decreased with increasing complexity of substituents.

Koppová[6] studied the hydrogenation of 1-, 2-, 3-, and 4-octynes on Pd on kiselguhr, silica gel and activated carbon in n-heptane and absolute alcohol. Substances with the triple bonds at the first and third carbon atoms were hydrogenated faster than those with the triple bonds at the even carbon atoms, and the hydrogenation rate was higher for 1-octyne than for 3-octyne. During the hydrogenation of 2-, 3-, and 4-octynes, the respective *cis*-olefins were first formed, whereas isomerization of the double bond towards the chain centre (predominantly to position 2), giving rise to the corresponding *cis*- and *trans*-olefins, took place to a higher extent during the hydrogenation of 1-octyne. The hydrogenations were faster in polar than in nonpolar solvents.

Červený, Skala and Růžička[7] investigated the competitive hydrogenation of 4--octyne and 1,3-cyclooctadiene over catalysts of Pt and Pd on activated carbon. The selectivity of the competitive hydrogenation, defined as the ratio of reactivity of 4-octyne to that of 1,3-cyclooctadiene, was higher on the platinum catalyst than on the palladium catalyst, and higher in hexane than in methanol on the two catalysts.

Summarizing these findings, we observe some inconsistency in the results so far obtained and in the conclusions derived from them, presumably due to the effect of factors that were considered insignificant, such as the nature of the catalyst support, medium, *etc.* This stimulated us to undertake the present study.

EXPERIMENTAL

Substances. The substrates were largely commercial chemicals: 1-hexyne, 2-hexyne, 3-hexyne, 3-heptyne, acetylenedicarboxylic acid dimethyl ester, 1,4-dichloro-2-butyne (Koch–Light Laboratories, U.K.), 2-heptyne, 1-octyne, 2-octyne, 3-octyne, 4-octyne (Schuchardt, F.R.G.), 1-nonyne, 1-decyne, 2-butyne-1,4-diol, 2,4-hexadiyne-1,6-diol, 1,3-cyclooctadiene, 1,3-cyclohexadiene, 1,4--cyclohexadiene (Fluka, Switzerland), 1,7-octadiene (Chemische Werke Hüls, F.R.G.). 1,5-Hexadien-3-ol was prepared[8] by reacting allyl magnesium bromide with acrolein and decomposing the adduct with water. All substrates were freshly distilled prior to use and were chromatographically pure. Methanol and n-hexane were commercial chemicals (Lachema, Brno), distilled prior to use.

The catalyst was Cherox 41-00 (Chemické závody ČSSP, Litvínov), which is 3% Pd on Supersorbon Degussa HB-3 activated carbon. A fraction with grain size smaller than 0·063 mm was used. Hydrogen was electrolytic, conforming to Czechoslovak Standard ČSN 65 4435 (Technoplyn, Kyje).

Apparatus and procedure. The measurements were performed[9] in an isothermal stirred batch reactor at 20°C and atmospheric pressure. The time dependence of hydrogen uptake was measured by using gas volumetric burettes; samples for chromatographic analysis were taken during the reaction. 50—150 mg of catalyst and 0·4 ml of substrate in 10 ml of solvent were used in the experiments.

Analytical methods. The analyses were carried out on a Chrom-4 apparatus with flame ioniza-
tion detection (Laboratorní přístroje, Prague). Several columns with different packings were
used in different conditions; the isothermal mode was preferentially employed. A survey of the
analyses is given in Table I. The analyses of the hydrogenation products of a substance or a mix-
ture of a pair of substances in methanol and hexane were largely performed using the same
chromatographic column under the same conditions; exceptions are marked in Table I by
reference to solvent.

RESULTS AND DISCUSSION

The experiments were performed using a single catalyst, *viz.* 3% Pd/activated carbon,
a polar (methanol) and a nonpolar (n-hexane) solvent, and a series of alkynic and
dienic substances. The substrates were hydrogenated either individually or competiti-
vely in pairs, which enabled the reaction rates (rate constants) and relative adsorption
coefficients to be evaluated. The experimental conditions used prevented the reaction
rates from being affected by mass transport[10].

TABLE I
Survey of chromatographic analyses

Column[a]	Hydrogenation reaction mixture (temperature, °C)
A	1-hexyne (65); 2-hexyne (70); 3-hexyne (75); 1-octyne (120); 3-octyne (120); 4-octyne (120); 1-nonyne (150); 1-decyne (160); 1-nonyne and 1-, 2-, 3- and 4-octynes in hexane (120); 1-hexyne and 1-decyne in hexane (80—150); 1,3- -cyclohexadiene and 1,4-cyclooctadiene in methanol (60); 1,3-cyclohexadiene and 1-hexyne (60); 1,3-cyclohexadiene and 3-hexyne (60)
B	1,3-cyclohexadiene (50); 1,4-cyclohexadiene (50); 1,3-cyclooctadiene (125); 1,5-cyclooctadiene (125); 1,7-octadiene (90); 1,3-cyclohexadiene and 1,4-cyclo- hexadiene in hexane (50); octadiene and 1-octyne (120)
C	2-heptyne (80); 3-heptyne (80)
D	acetylenedicarboxylic acid dimethyl ester (175); acetylenedicarboxylic acid dimethyl ester and 1-decyne (60—165); acetylenedicarboxylic acid dimethyl ester and 4-octyne (60—165)
E	2-butyne-1,4-diol (200); 2-butyne-1,4-diol and 1-decyne in methanol (200)
F	1-nonyne and 1-, 2-, 3- and 4-octynes in methanol (80); 1-hexyne and 1-decyne in methanol (80—150)

[a] A — 15% PEG 1 540 on Chromosorb P (4 m); B — 15% Reoplex 400 on Chromaton N-AW-
-DMCS (2·4 m); C — 5% Tween 80 on Chromaton N-AW-HMDS (2·4 m); D — 5% XE 60
on Chromaton N-AW-DMCS (2·4 m); E — Tenax GC (1·2 m); F — 10% diethylene glycol
succinate on Chromaton N-Super (2·4 m).

The hydrogenations of the individual substrates proceeded at constant rates. In some instances, the plots of time dependence of hydrogen takeup exhibited breaks in the range of takeup of 1 mol of hydrogen *per* mol of substrate, after which the hydrogenation proceeded at a lower, again constant, rate as far as the theoretical hydrogen consumption. Such hydrogenations were selective and the rate of the consecutive hydrogenation of the olefin formed could be derived from a single experiment.

The reaction rates are given in Table II. The hydrogenations were generally faster in methanol than in hexane. The dependence of the hydrogenation rate on the

TABLE II
Alkyne and diene hydrogenation rates

| Substance | Hydrogenation rate, ml_{H_2} min^{-1} g_{cat}^{-1} | | | |
| | in methanol | | in hexane | |
	initial	consecutive	initial	consecutive
1-Hexyne	120	—[a]	86	—[a]
2-Hexyne	110	60	112	24
3-Hexyne	174	74	124	40
2-Heptyne	104	16	96	28
3-Heptyne	172	48	144	32
1-Octyne	160	—[a]	120	—[a]
2-Octyne	144	34	102	18
3-Octyne	170	80	134	82
4-Octyne	121	80	8	32
1-Nonyne	180	—[a]	136	—[a]
1-Decyne	154	—[a]	104	—[a]
2-Butyne-1,4-diol	50	—[a]	—[b]	—[b]
1,4-Dichloro-2-butyne	130	—[a]	100	—[a]
Acetylenedicarboxylic acid, dimethyl ester	166	—[a]	60	—[a]
2,4-Hexadiyne-1,6-diol	48	—[a]	—[b]	—[b]
1,3-Cyclohexadiene	160	—[a]	120	—[a]
1,4-Cyclohexadiene	90	—[a]	58	—[a]
1,3-Cyclooctadiene	148	20	110	15
1,5-Cyclooctadiene	84	—[a]	46	—[a]
1,7-Octadiene	180	70	80	20
1,5-Hexadien-3-ol	120	60	60	15

[a] Reaction is nonselective, reaction rate change in the range of takeup of 1 mol of hydrogen *per* mol of hydrogenated substance is not sharp; [b] substance is sparingly soluble in this solvent.

alkyne structure proved to be more complex than in the case of olefins[11]. For instance, in the series of 1-alkynes the reaction rates in both solvents decreased in order $C_9 > C_8 > C_{10} > C_6$; the corresponding 1-alkenes were formed and underwent not only consecutive hydrogenation but also isomerization giving both the *cis*- and *trans*-2-alkenes.

Alkynes with the triple bonds in position 3 were hydrogenated faster than those with the same numbers of carbon atoms and the triple bonds in position 1, 2 or 4. The *cis*-olefins formed by hydrogenation of alkynes with inner triple bonds behaved likewise. In these cases the hydrogenation was selective, so that the hydrogenation rates of both the alkyne and the *cis*-olefin formed from it could be determined from the time dependence of hydrogen takeup. The hydrogenation of the *cis*-olefin was accompanied by the formation of the *trans*-isomer which was hydrogenated as well. In the case of 1-alkynes the hydrogenation was not selective, no sharp break (drop) of the reaction rate being observed in the range of takeup of 1 mol of hydrogen *per* mol of substrate.

Hydrogenation of substituted alkynes containing substituents with hetero atoms (—OH, —Cl, —COOCH₃) was not selective either. Alkynic diols in methanol were hydrogenated rather slowly; in hexane the measurements were precluded by the low solubility of the substances to be hydrogenated. For 2,4-hexadiyne-1,6-diol the hydrogenation rate decreased with time, being thus indicative of nonselectivity of this hydrogenation. The hydrogenation of 1,4-dichloro-2-butyne was associated with the hydrogenolytic elimination of chlorine in the form of hydrogen chloride, which appeared in an increased acidity (observed by means of indicator papers) and a decreasing reaction rate. In this case the initial reaction rates were determined as the slopes of the tangents to the curves of time dependence of hydrogen takeup in time $t = 0$.

The hydrogenation of 1,3- and 1,4-cyclohexadiene was accompanied by the formation of benzene, presumably following the pathway shown in Scheme 1.
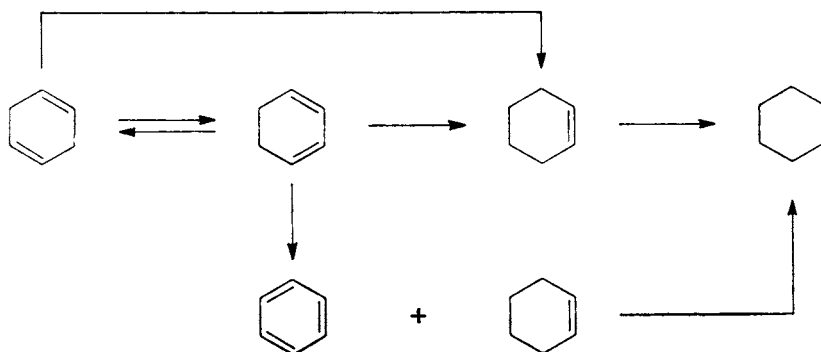
SCHEME 1

About 30% of the starting diene was converted so to benzene by disproportionation; the latter was not subject to hydrogenation in the conditions used. 1,3-Cyclohexadiene was not detected in the reaction mixture from the hydrogenation of 1,4-cyclohexadiene, its transient formation, however, is prerequisite in the concept accounting for the formation of benzene. During the hydrogenation of 1,5-cyclooctadiene, the double bond isomerized to give the thermodynamically more favourable 1,3-isomer, presumably *via* 1,4-cyclooctadiene. The hydrogenation of 1,3-cycloctadiene was selective, so that the rate of the consecutive hydrogenation of cyclooctene could be determined. Cyclic 1,3-dienes with larger rings were hydrogenated at lower rates. The hydrogenation of cyclic dienes with more distant double bonds was nonselective and slower than that of conjugated cyclic dienes with the same number of carbon atoms. The hydrogenation of 1,7-octadiene, a diene with isolated double bonds in the terminal positions of the chain, was relatively fast and selective; the analogous dienic alcohol, 1,5-hexadien-3-ol, also hydrogenated selectively but more slowly.

Hydrogenations of equimolar mixtures of pairs of alkynic and dienic substrates were also investigated. The pairs were chosen so as to enable the course of the competitive hydrogenations to be monitored analytically and the effect of structure on the adsorptivity of the substances to be evaluated. The selectivities were expressed by means of the Rader–Smith relation[12]

$$S_{A,B} = r_A/r_B = k_A K_A/k_B K_B = \log(C_A/C_A^0)/\log(C_B/C_B^0) \qquad (1)$$

which is based on the assumption that the adsorption terms in the kinetic equations for the hydrogenation of the individual substrates are the same. This relation has been applied with success[2] to the evaluation of hydrogenations of a number of pairs of substances of the same kind. It did not suit to the description of alkyne–olefin and diene–olefin systems[13,14] (the $\log(C_A/C_A^0)$ *vs* $\log(C_B/C_B^0)$ plots were not linear), but it fitted well alkyne–diene systems[7].

The dependences measured were transformed to the Rader–Smith coordinates, and linear relations were invariably obtained for the time that both of the alkynic or dienic substances were present in the system. Similarly as in paper[15], the instantaneous concentrations of the alkynes or dienes relative to their initial concentrations were plotted irrespective of the composition of the reaction products. Using the initial reaction rates in place of the rate constants k_A and k_B, the relative adsorption coefficients were calculated by means of the selectivities of the competitive hydrogenations read from the plots; the data are given in Table III.

This table shows that neither the effect of the carbon chain length on the adsorptivities of 1-alkynes (C_6—C_9) nor the solvent effect is very marked. An appreciable difference occurs between the adsorptivities of 1-alkynes and alkynes with internal triple bonds; the adsorptivity decreases as the triple bond shifts towards the centre of the molecule of octyne, the difference between 3-octyne and 4-octyne being not

very pronounced. The directly measured relative adsorption coefficients of 3- and 4-octynes agree well with those obtained by calculation from adsorptivity measurements of the two substances in mixtures with 1-nonyne (0·8 and 0·71, respectively).

Competitive hydrogenations of alkynes containing substituents with hetero atoms (2-butyne-1,4-diol and acetylenedicarboxylic acid dimethyl ester) and normal alkynes (1-decyne, 4-octyne) confirmed a higher adsorptivity of 1-alkynes as compared to alkynic substances with their triple bonds inside the chain. A marked solvent effect was observed: In methanol, acetylenedicarboxylic acid dimethyl ester started to be hydrogenated only after 1-decyne was completely spent, whereas in hexane the two substances were hydrogenated simultaneously, although 1-decyne considerably faster. In a mixture with 4-octyne in methanol, acetylenedicarboxylic acid dimethyl ester was similarly hydrogenated only after a complete takeup of the octyne whereas in

TABLE III
Relative adsorption coefficients

Competitive hydrogenated substances		Relative adsorption coefficient K_A/K_B in	
A	B	methanol	hexane
3-Hexyne	1-hexyne	0·12	—
1-Decyne	1-hexyne	0·95	0·94
1-Octyne	1-nonyne	—	1·00
2-Octyne	1-nonyne	—	0·42
3-Octyne	1-nonyne	—	0·12
4-Octyne	1-nonyne	0·21	0·17
2-Butyne-1,4-diol	1-decyne	0·19	—
Acetylenedicarboxylic acid, dimethyl ester	1-decyne	0	0·09
3-Octyne	4-octyne	—	0·80
Acetylenedicarboxylic acid, dimethyl ester	4-octyne	0	0·50
1-Hexyne	1,3-cyclohexadiene	6·2	—
3-Hexyne	1,3-cyclohexadiene	0·67	—
3-Octyne	1,3-cyclooctadiene	3·4	2·8
3-Octyne	1,5-cyclooctadiene	6·2	5·0
1,4-Cyclohexadiene	1,3-cyclohexadiene	0·21	0·26
1,3-Cyclooctadiene	1,3-cyclohexadiene	—	0·15
1,5-Hexadien-3-ol	1,3-cyclohexadiene	0	0
1,7-Octadiene	1,3-cyclooctadiene	0·62	0·77
1,4-Cyclohexadiene	1,5-cyclooctadiene	—	3·0

hexane the two substances were hydrogenated at commensurable rates. Solvent effect of this kind has been observed for alkynic[16] and olefinic[2,11] substrates previously. Presumably, interactions of the polar solvent with polar groups of the substance with substituents bring about a weakening of adsorptivity of the latter, hence, an increase in the relative reactivity of the other substance, not containing polar substituents.

Competitive hydrogenations of mixtures of alkynes with cyclic dienes possessing the same number of carbon atoms showed that the two substances are hydrogenated simultaneously, the reactivity of the alkyne being favoured slightly by the polar solvent. The reverse solvent effect has been observed[7] for the competitive hydrogenation of 4-octyne with 1,3-cyclooctadiene. The solvent effect is small anyway and cannot be compared with that in case that one of the reactants carries some polar group. The calculated relative adsorptivities of 1-hexyne and 3-hexyne were again consistent with the directly measured values (0·11 and 0·12, respectively). The calculation also revealed a higher adsorptivity of 1,3-cyclooctadiene, where the two double bonds are in conjugation, as compared to the 1,5-isomer. Higher adsorptivities of conjugated systems were also found by direct measurements on 1,3- and 1,4-cyclohexadienes. Cyclic dienes with larger rings exhibited lower adsorptivities; this applied to conjugated (1,3-cyclooctadiene and 1,3-cyclohexadiene) as well as unconjugated (1,4-cyclohexadiene and 1,5-cyclooctadiene) systems. 1,5-Hexadien--3-ol was only hydrogenated after a complete hydrogenation of 1,3-cyclohexadiene in both solvents. This is clearly due to a negative effect of the —OH group on the adsorptivity of 1,5-hexadien-3-ol, because 1,7-octadiene, whose double bonds are also located at the terminal groups of the chain, underwent competitive hydrogenation in a mixture with 1,3-cyclooctadiene.

Tables II and III demonstrate that in nearly all cases the substances studied differ more in their relative adsorption coefficients than in their relative hydrogenation rates pertaining to the reactions of the individual substrates; this implies that the selectivity of competitive hydrogenations is determined primarily by the relative adsorptivity of the reactants.

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