CATALYTIC HYDROGENATION OF BINARY AND TERNARY MIXTURES OF UNSATURATED SUBSTANCES IN THE LIQUID PHASE ON PLATINUM

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Hydrogenation of olefinic substrates in binary and ternary mixtures using 5% Pt on silica gel as the catalyst was studied in normal conditions in the liquid phase with methanol or cyclohexane or in solvent-free systems. The effect of the solvent concentration on the selectivity of hydrogenation of the unsaturated alcohol–olefin binary mixtures was investigated. In ternary systems of unsaturated substrates, the effect of each of the substrates on the selectivity of hydrogenation of the remaining two substances was examined. Another system was found in which a jump change of the hydrogenation selectivity occurred on the vanishing of the fastest reacting substance.

In our previous works[1-4] it has been ascertained that an addition of a third substance to a hydrogenated binary mixture of olefinic substrates can in many cases affect significantly the selectivity of hydrogenation of this mixture. This effect was most appreciable in systems olefin–unsaturated alcohol[1] and occurred in cases that the third component in comparable concentration was an unsaturated substance[4,5], which adsorbed competitively and reacted on the catalyst's surface, as well as in cases that the third substance was a classical solvent, which did not adsorb competitively (was not involved in the Langmuir–Hinshelwood type equations, which thus degraded to pseudo-zero order) and exerted its influence obviously *via* interactions of the molecules from the bulk phase with the adsorbed substrate molecules. When the nature of the third substance added approached that of one of the binary mixture components, the selectivity shifted always in favour of the other, chemically different component[1,4,5]. Classical solvents have been so far employed[1,6] always in concentrations multiply exceeding those of the olefinic substrates added (25 ml per 1 ml of the mixture to be hydrogenated), while the effect of the third olefinic substrate on the selectivity of hydrogenation of a binary olefinic mixture could only be examined for comparable concentration of all three substrates, as the application of one olefinic substrate in a high excess would bring about its preferential hydrogenation.

In the present work, the effect of classical solvents – methanol and cyclohexane – on the selectivity of hydrogenation of binary olefinic mixtures was studied in systems in which the concentration of the solvent was comparable with those of the olefinic substrates. The hydrogenation rate was in all cases zero order with respect to the concentration of the unsaturated substance. Furthermore, the course of the competitive hydrogenation was examined in ternary olefinic systems. The effect of an olefinic substrate on the selectivity of hydrogenation of the two other substances was investigated.

EXPERIMENTAL

Substances used. The catalyst, 5% Pt on silica gel, was prepared as described previously[6]; the fraction grain size below 0·063 mm was employed. The hydrogen was electrolytical and was used without further treatment. The substrates were commercial chemicals, 1-propenyl phenyl ether, 2-methyl-2-propen-1-ol, 2-methyl-3-buten-2-ol (Koch-Light Labs., Great Britain), 4-methyl-2-pentene (Fluka, Switzerland), 2-propen-1-ol, 1-hexene (Lachema, Brno — imported); *trans*-2-buten-1-ol was prepared according to ref.[7] Cyclohexane and methanol (Lachema, Brno) served as the solvents. All the substrates and solvents were distilled prior to use and were chromatographically pure.

Apparatus and measurement techniques. The hydrogenations were accomplished at 20°C at atmospheric pressure of hydrogen using the apparatus described previously[4]. The reactor was stirred by means of a magnetic stirrer, the amount of the catalyst was 0·08 g, and 1·5 ml of the binary or ternary olefinic mixture or 1 ml of the binary olefinic mixture with 1 ml of the solvent were always subject to hydrogenation. An analogous reactor of the volume of 40 ml was employed for handling 25 ml of the solvent. Samples of about 20 μl were taken during the reaction and gas chromatographically analyzed.

The analyses were performed on instruments Chrom 2 and Chrom 4 with flame ionization detection. Glass columns, length 2—4 m, i.d. 2·5 mm were used, packed with 15% Carbowax 20 M, 10% PEG 6000 and 10% $AgNO_3$ + ethylene glycol on Chromaton NAW, gain size 0·16—0·20 mm. The packing type and the temperature (in the region 30—150°C) were chosen always with respect to the composition of the mixture analyzed.

RESULTS AND DISCUSSION

The effect of the third substance C on the hydrogenation of two unsaturated substrates A and B was evaluated by employing the selectivity values obtained by the competitive reactions method according to Rader and Smith[8]. The various overall degrees of conversion lay in the region of 0·35 to 0·80 according to the absolute hydrogenation rates. A series of selectivities of hydrogenation of unsaturated alcohol–olefin mixtures without the presence of a third component and those pertaining to these mixtures in the presence of methanol or cyclohexane in different amounts were obtained as given in Table I.

When methanol was applied, the selectivity values for the hydrogenation of the unsaturated alcohol and olefin decreased virtually in all cases, in accordance with the results of our previous work[1]. In some instances, the selectivities for high methanol concentrations were somewhat higher than for concentrations comparable with those of the unsaturated substrates; the differences, however, were not so significant as the decrease of the hydrogenation selectivity in the presence of methanol in comparison with the values measured for the corresponding binary mixtures without the solvent.

With cyclohexane as the solvent, the selectivity of hydrogenation of the unsaturated alcohol and olefin increased in systems involving 1-hexene, in accordance with the work[1]. The selectivity rose appreciably with the increasing concentration of the solvent. Systems with 4-methyl-2-pentene were not applied, since the selectivities of hydrogenation of the binary mixtures themselves were very high and a further increase, which was expected, in fact could not be monitored experimentally[5].

The order of the reactivities of the unsaturated alcohols with respect to 1-hexene was not the same as that with respect to 4-methyl-2-pentene (Table I), from which it follows that the relative reactivities of different alcoholic substrates with respect to an olefinic substrate depend not only on the structure of the former, but also on the structure of the latter. In both series, the most reactive was 2-propen-1-ol, a substance with a monosubstituted double bond and a hydroxy group bonded at the carbon atom adjacent to the double bond. The other three unsaturated alcohols used differed by the number of substituents at the double bond, or the number of substituents at the carbon atom at which the hydroxy group is bonded. An increase of the number of substituents is in both cases accompanied by a decrease of the hydrogenation reactivity[1,4,5], its extent, however, depends also on the structure of the reference substrate. As is apparent from Table I and from the previous works[1,4,5], the relative reactivity can be significantly affected by the solvent, and generally, of course, also by the catalyst.

TABLE I

Selectivities of Hydrogenation of Olefinic Substrates in Binary Mixtures and in the Presence of Solvents

System[a]		$S_{A,B}$	$S_{(A,B)C}$			
			C = methanol		C = cyclohexane	
A	B		1 ml	25 ml	1 ml	25 ml
N	M	0·98[b]	0·41	0·46	1·35	5·56
G	M	0·32	0·26	0·32[c]	0·81	7·70
H	M	0·43	0·12	0·26[c]	0·59	6·60
I	M	3·82	2·40	1·46	5·26	66·80
N	L	32	6·25	12·5	—	—
G	L	40	7·75	8·6	—	—
H	L	541[b]	6·33	15·9	—	—
I	L	1 600[b]	26·00	63·0	—	—

[a] Symbols used for the substrates: G 2-methyl-2-propen-1-ol, H 2-buten-1-ol, I 2-propen-1-ol, L 4-methyl-2-pentene, M 1-hexene, N 2-methyl-3-buten-2-ol; [b] ref.[5]; [c] ref.[1].

TABLE II

Hydrogenation Selectivities Measured in Ternary Systems

System[a] A	B	C	$S_{A,B}$	$A_{(A,B)C}$	$S_{(B,C)A}$	$S_{(C,A)B}$	Product[b]
G	M	N	0·32	0·15	6·67	0·93	0·96
G	M	H	0·32	0·24	3·89	1·13	1·05
G	M	F[c]	0·32	0·74	0·56	2·33	0·97
H	M	N	0·43	0·14	2·34	3·58	1·17
H	M	I	0·43	0·23	0·79	5·56	1·01
H	M	F	0·43	0·72	0·59	2·47	1·04
N	M	F	0·98	1·03	0·52	1·90	1·01
I	M	G	3·82	4·54	3·70	0·064	1·08
I	M	F	3·82	5·29	0·72	0·27	1·02
N	L	F	32	2·68	0·12	3·12	1·00
G	L	N	40	0·50	1·17	1·69	0·98
G	L	H	40	12·66	0·18	0·72	1·64
G	L	I	40	23·36	0·71	0·065	1·09
G	L	F	40	99·20	0·002	3·87	0·77
H	L	I	541	0·32	0·32	5·80	1·00
H	L	N	541	7·26	0·057	2·43	1·00
H	L	F	541	7·63	0·03	4·45	1·01
I	L	N	1 600	1·15	0·65	1·27	0·95
I	L	F	1 600	6·25	0·76	0·23	1·09

[a] Symbols used as in Table I, F 1-propenyl phenyl ether; [b] product of the values $S_{(A,B)C}$ $S_{(B,C)A}$ $S_{(C,A)B}$; [b] ref.[5].

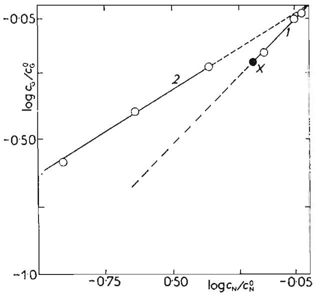

FIG. 1

Changes of Concentrations of 2-Methyl-2-propen-1-ol (G) and 2-Methyl-3-buten-2-ol (N) During the Competitive Hydrogenation in the Ternary Mixture with 1-Hexene (M)

Furthermore, the effect of various unsaturated substrates (unsaturated alcohols and 1-propenyl phenyl ether) on the selectivity of hydrogenation was investigated for a series of pairs unsaturated alcohol–olefin. 57 values of hydrogenation selectivities were thus obtained for pairs of substrates in ternary systems, listed in Table II. The selectivities for the binary systems, given in Table I, are here shown for a comparison too. The values obtained satisfied well the relation

$$S_{(A,B)C}\, S_{(B,C)A}\, S_{(C,A)B} = 1\,. \tag{1}$$

In cases that the substances A and C were unsaturated alcohols and B was an unsaturated hydrocarbon, the selectivity for the substance A and B was lower in the presence of the substance C as compared with the binary system ($S_{(A,B)C} < S_{A,B}$) in all instances save the system* I, M, G, where the $S_{(I,M)G}$ value was somewhat higher than the $S_{I,M}$ value. This general finding is in accordance with the conclusion[5] that the selectivity of hydrogenation of two chemically different unsaturated substances (unsaturated alcohol–olefin) changes in the presence of a third substance whose nature approaches that of one of the two components (unsaturated alcohol) in such a manner that in the ternary system the hydrogenation of that substance which differs chemically from the third substate added is favoured as compared with the hydrogenation of the binary system. The presence of 1-propenyl phenyl ether in the reaction mixture did not bring about changes in the hydrogenation selectivities for the unsaturated alcohol–olefin systems such as would lead to generally valid conclusions.

In the system M, G, N the fastest reacting substance, M, vanished in an acceptable time (see the point X in Fig. 1). The concentrations of the substances G and N changed in the presence of the substance M along the straight line *1*, which is characterized by the slope $D_{(G,N)M} = 1{\cdot}07$. At the instant when the substance M vanished, the selectivity altered and the concentrations of the reacting components varied then along the straight line 2. The hydrogenation selectivity in this region, 0·63, approached the value measured in the binary system, $S_{G,N} = 0{\cdot}73$. n-Hexane, formed on the hydrogenation of 1-hexene, thus in a concentration comparable with that of the reacting substances does not exert such a marked effect upon the selectivity of hydrogenation of a binary mixture of two unsaturated alcohols as 1-hexene. A similar observation has been made in the work[5]. The results indicate that an unsaturated substance, adsorbing on the surface of the catalyst, has a greater influence on the selectivity of hydrogenation of two other substrates than a saturated substance of the same skeleton, affecting the process only *via* interactions from the bulk phase.

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* For the symbols used see the footnote[a] to Table I.

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