EFFECT OF SOLVENTS ON THE COURSE
OF COMPETITIVE HYDROGENATIONS*

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An attempt is presented to express the influence of solvents on the relative adsorptivity of unsaturated substrates in their catalytic hydrogenations, namely on the basis of linear relations of free enthalpies. The hydrogenation of cyclohexene, 1-hexene, 2-methyl-3-buten-2-ol, and 2-propen-1-ol over the 5% platinum on silica gel catalyst has been examined in 19 solvents under ordinary conditions. The relative adsorption coefficient values in particular solvents have been measured by the method of competitive reactions. For the quantitative expression of the solvent effect on the relative adsorptivity a semiempiric equation has been proposed similar to the earlier modified Drougard–Decroocq equation concerning the influence of solvents on the rate of catalytic hydrogenations.

As demonstrated in numerous papers, the selectivity of heterogeneously catalysed reactions may be markedly influenced by the choice of solvents. For a detailed examination and prediction of this effect, it would be desirable to gather informations on the influence of solvents on the adsorption coefficients of the particular reactants. In this respect, the method of competitive reactions represents an advantageous route to obtain the required data since the inaccuracy of measurements is compensated by distribution of errors on all the occurring reactions. The results may be interpreted with the use of Langmuir kinetics on the basis of the equation proposed by Rader and Smith[1]. The latter equation makes possible to calculate the relative adsorption coefficients from data obtained in the competitive reaction and from rate constants of the individual reactions in the zero-order region with respect to the concentration of the substrate. In the hitherto published papers from this field of chemistry, differences have been reported in relative substrate adsorptivities in competitive hydrogenations[2-9] on various catalysts under various conditions.

In this paper, an attempt is presented to express quantitatively the influence of solvents on the relative adsorptivity of hydrogenated substrates. For the correlation there was used equation (1) analogous to the earlier[10] proposed modified Drougard–Decroocq correlation of rate constants.

$$\log \left(K_{A,B}\right)_n / \left(K_{A,B}\right)_0 = \gamma \varphi . \qquad (1)$$

Parameters φ were defined under the presumption that $\gamma = 1$ for the model pair of substrates A and B (A, 2-methyl-3-buten-2-ol; B, 1-hexene) using methanol as the standard solvent ($\varphi = 0$). The use of equation (1) was then examined in hydrogenations of some other pairs of substrates over the same catalyst and under the same conditions. The present equation (1) represents a further type of linear correlations of free enthalpies from which the Hammett[11] and Taft[12] equation have been most widely used. The original applicability range of these correlations in homogeneous reactions has been successfully extended to the field of heterogeneous catalysis[13]. Along with the earlier defined[1,14,15] τ' values, the φ values represent a valuable parameter characteristic of the influence of the solvent in heterogeneously catalysed hydrogenations. For further generalisations, additional sets of consistent experimental data are required.

EXPERIMENTAL

Materials. The 5% platinum on silica gel catalyst[16] was prepared according to ref.[10]; the particle size of less than 0·063 mm was used in measurements. For the solvents and their purification and purification of hydrogen see the same ref.[10]. As compounds to be hydrogenated, there were used the commercial preparations of 1-hexene, 2-methyl-3-buten-2-ol (Koch-Light, Great Britain), and 2-propen-1-ol (Lachema, Brno, Czechoslovakia); cyclohexene was prepared by dehydration of cyclohexanol on alumina[17]; all these substrates were purified by distillation prior to the measurements.
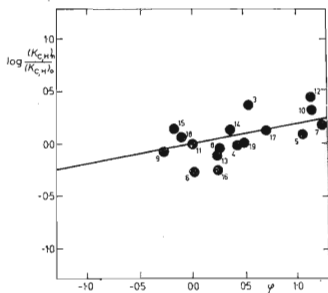

FIG. 1

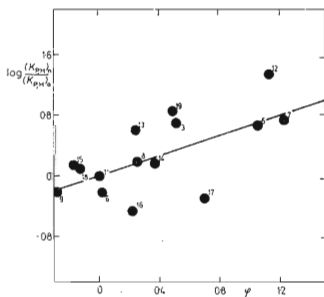Correlation of Relative Adsorption Coefficients of Cyclohexene and 1-Hexene with φ Solvent Constants

FIG. 2

Correlation of Relative Adsorption Coefficients of 2-Propen-1-ol and 1-Hexene with φ Solvent Constants

Apparatus and procedure. The hydrogenations were performed at the temperature of 20°C and atmospheric pressure of hydrogen in a stirred all-glass reactor[18] equipped by a device for withdrawal of samples by means of a syringe without the interruption of the stirring. This reactor was used instead of the earlier[10,19] rocking vessel in a standard apparatus. Hydrogenations of individual substrates (1 ml) and of binary mixtures (2—4 ml of an equimolar mixture) were performed in 25 ml of the particular solvent over 0·1—0·2 g of the catalyst depending on the absolute hydrogenation rates in particular solvents. In the course of the hydrogenation, samples (volume, about 0·1 ml) were withdrawn in suitable time intervals for the sake of chromatographic analysis.

Analytical methods. Chromatographic analyses of reaction mixtures were performed on a Chrom-2 apparatus (flame-ionisation detector) using the following three types of columns: 1, 4 m of length, 2·5 mm of internal diameter, packed with 15% poly(ethylene glycol) 6000 on Chromaton N—AW, particle size 0·2—0·25 mm; 2, 2·8 m of length, 2·5 mm of internal diameter, packed with 20% poly(ethylene glycol) 600 on Chezasorb; and 3, 3 m of length, 2·5 mm of internal diameter, packed with 15% Silikongummi für Gaschromatographie (Merck) on Chromaton N—AW HMDS, particle size 0·16—0·20 mm. Temperature range: 60—90°C.

TABLE I

Relative Adsorption Coefficient of Hydrogenation Substrates in Various Solvents

No[a]	Solvent	φ	$K_{C,H}$	$K_{D,H}^b$	$K_{D,C}^c$	$K_{P,H}$	$K_{D,P}^d$	$K_{D,P}$
1	hexane	—	—	—	—	192		
2	cyclohexane	0·782	—	2·54		41·1	0·062	0·060
3	dibutyl ether	0·509	0·35	1·36	3·87	86·2	0·016	—
4	diethyl ether	0·431	0·14	1·14	7·99	14·0	0·081	0·050
5	cumene	1·076	0·19	5·03	27·00	81·9	0·061	—
6	1-butanol	0·018	0·08	0·44	5·26	11·2	0·039	—
7	ethylbenzene	1·229	0·22	7·15	31·92	93·9	0·076	—
8	1-propanol	0·258	0·14	0·76	5·51	26·4	0·029	—
9	ethanol	−0·285	0·13	0·22	1·73	11·1	0·020	0·012
10	toluene	1·144	0·33	5·88	18·04	→∞	→0	—
11	methanol	0·000	0·15	0·42	2·75	17·9	0·024	0·028
12	benzene	1·137	0·64	5·78	13·29	394·0	0·015	0·024
13	ethyl acetate	0·242	0·12	0·74	6·34	71·9	0·010	0·035
14	tetrahydrofuran	0·370	0·21	0·99	4·70	24·2	0·041	—
15	dioxane	−0·178	0·22	0·28	1·29	23·8	0·012	—
16	benzyl alcohol	0·223	0·08	0·70	8·26	4·9	0·144	—
17	diethyl malonate	0·709	0·21	2·16	10·44	8·7	0·248	—
18	ethyl benzoate	−0·123	0·18	0·32	1·81	23·6	0·014	—
19	1,1,2,2-tetrachlorethane	0·485	0·15	1·29	8·61	116·9	0·011	—

[a] The solvent numbering is identical with that in Figs 1—3; [b] basis of definition; [c] calculated from experimental $K_{D,H}$ and $K_{C,H}$ values; [d] calculated from experimental $K_{D,H}$ and $K_{P,H}$ values.

Most analyses were performed on column 1; only toluene and propanol could not be removed on this column. Toluene was removed through column 2 and propanol with the use of column 3.

RESULTS AND DISCUSSION

Kinetic measurements were performed under those conditions when the reaction rate was not influenced by mass transport[10]. The external diffusion effect was excluded by efficient stirring (540−1040 revolutions per min) while the internal diffusion was excluded by a sufficiently small particle size of the catalyst (less than 0·063 mm). The volumetrically determined rates were corrected to the partial hydrogen tension of 760 Torr with respect to the solvent tension under the assumption of a first-order reaction with regard to the hydrogen concentration[10]. Competitive hydrogenations were always performed two times. Through the resulting set of points of the $\log \left(c_A/c_A^0\right)$ vs $\log \left(c_B/c_B^0\right)$ relation a straight line was drawn, the slope[20] of which is defined by the relation (2)

$$S_{A,B} = \left(k_A/k_B\right) K_{A,B} . \tag{2}$$

As the k_A and k_B values there were used experimental reaction rates of the zero-order region (with respect to the substrate concentration). The calculated relative adsorption coefficient values are shown in Table I.

Interpretation of thus-obtained data is rather difficult. The attempted correlation in $\log K_{A,B}$ coordinates with kinetic parameters of both the original[21] and modified[10] Drougard–Decroocq equation was not successful. Correlations with some selected physico-chemical solvent properties such as dielectric constant, dipole moment, and molar polarisation, did not meet with success. Best results have been obtained in applications of the newly proposed equation (1). The corresponding correlations are

TABLE II

Parameter γ and Correlation Coefficient r_{xy} Values

System	γ	r_{xy}
Cyclohexene–1-hexene	0·20	0·56
2-Methyl-3-buten-2-ol-1-hexene[a]	1·00	1·00
2-Methyl-3-buten-2-ol-cyclohexene	0·81	0·76
2-Propen-1-ol–1-hexene	0·66	0·61
2-Methyl-3-buten-2-ol-2-propen-1-ol	0·36	0·38

[a] Basis of definition.

shown on Figs 1–3. The calculated (linear regression method) γ parameter values and correlation coefficient values of the corresponding relations are shown in Table II. Table I indicates an interesting influence of the substrate structure on the adsorptivity. In all solvents of the present set, the strongest adsorptivity has been exhibited by 2-propen-1-ol while the adsorptivity of cyclohexene was the weakest. The adsorptivity of 1-hexene and 2-methyl-3-buten-2-ol was similar and varied with solvents to a considerable extent. The lowest adsorptivity of cyclohexene might be explained by involvement of a disubstituted double bond. In the case of 2-propen-1-ol and 1-hexene, the adsorptivity appears to be favourably influenced by the presence of the OH group at the α-carbon atom of the double bond system. On the other hand, the adsorptivity of 2-methyl-3-buten-2-ol is probably lowered by the steric effect of methyl groups. More accurate conclusions would require a greater set of model compounds to be hydrogenated.

The considerable effect of functional groups on the relative adsorptivity of substrates in various solvents may also be inferred from the present systems. In the case of unsaturated compounds of a similar character, such as cyclohexene–1-hexene, or, 2-methyl-3-buten-2-ol–2-propen-1-ol, the solvent effect was less significant than in systems unsaturated hydrocarbon–unsaturated alcohol. To obtain a wider spectrum of φ values, 2-methyl-3-buten-2-ol–1-hexene was used as the definitive system.

The interaction between the solvent and the adsorbed substrate obviously exerts considerable influence on the strength of the substrate – catalyst bonding. In alcoholic solvents, there is relatively preferred the adsorption of unsaturated hydrocarbons (low values of the φ parameter) while the adsorption of unsaturated alcohols is favoured in aromatic solvents (high values of φ). Generalisation of equation (1) would require additional experimental material. The validity of equation (1) can be
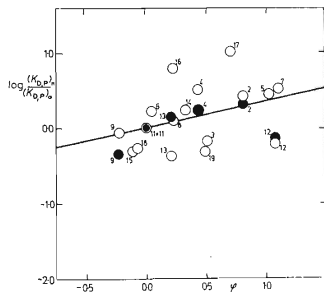

FIG. 3

Correlation of Relative Adsorption Coefficients of 2-Methyl-3-buten-2-ol and 2-Propen-1-ol (calculated from other measurements) with φ Solvent Constants

● Experimental values, ○ calculated values.

particularly assumed in series of pairs of structurally related substrates. It remains to verify the potential use of φ parameters in correlations between the solvents and the relative adsorptivity of substrates also in the case of some other double bond substituents or in hydrogenations of some other functional groups. Investigations in this respect are in progress.

LIST OF SYMBOLS

c	concentration, mol per litre
k	rate constant (dimension according to the rate equation)
$K_{A,B}$	relative adsorption coefficient of compounds A and B
r_{xy}	correlation coefficient
S	selectivity factor as defined by equation (2)
γ	parameter of equation (1) characteristic of the change of relative adsorptivity on the change of solvent
φ	parameter of equation (1) characteristic of the solvent effect on the relative adsorption coefficient of the two substrates

Subscripts

A, B	general designation of substrates to be hydrogenated
C	cyclohexene
D	2-methyl-3-buten-2-ol
H	1-hexene
P	2-propen-1-ol
n	the n solvent
o	solvent (methanol) selected as basis of the correlation

Superscripts

o	initial

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