

EFFECT OF SOLVENTS ON HYDROGENATION OF OLEFINIC SUBSTRATES*

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The presented work is a continuation of earlier studies and it is aimed at a quantitative interpretation of relations between the nature of a solvent and the rate of hydrogenation and adsorptivity of nine olefinic substrates. Hydrogenation experiments were performed at normal conditions in seven solvents with a catalyst containing 5% Pt on silica gel. Simultaneously, relations between the structure of substrates and their reactivity and adsorptivity in separate solvents were tested.

For quantitative interpretation of the effect of solvents on the rate of catalytic hydrogenation of the double bond and on the relative adsorptivity of olefinic substrates, the following equations have been proposed¹⁻³:

$$\log(k_{i,n}/k_{i,0}) = \lambda'\tau', \quad (1)$$

$$\log(K_{i,j,n}/K_{i,j,0}) = \gamma\varphi. \quad (2)$$

The values of constants τ' and φ , which characterize the influence of the solvent on the rate of hydrogenation resp. adsorptivity of hydrogenated substrates, have been evaluated by using selected model reactions. In an attempt to generalize these relations, their validity can be checked essentially by the three following methods: 1) for other catalysts or carriers, 2) for hydrogenation of other functional groups or 3) for hydrogenation of the double bond with further model substances containing other substituents. The third method seems to be the least painstaking transition and so we had decided to use it in our work. Besides the solvent, the structure of olefinic substrates had become a further variable.

EXPERIMENTAL

Materials used. The catalysts containing 5% Pt on silica gel was prepared⁴ similarly as in work¹. The mesh fraction <0.063 mm was used for the measurements. Commercial 1-hexene, allyl

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phenyl ether, allylbenzene, 2-methyl-2-propene-1-ol, 1-heptene-4-ol (Koch-Light, London) and ethylacrylate (Loba-Chemie, Wien) as well as synthesized substrates were used; 3-butene-1-ol was prepared by the Grignard reaction from allylmagnesium bromide and formaldehyde⁵, 3-butene-2-ol from methylmagnesium iodide and acrolein⁶ and 2-butene-1-ol (a *cis* + *trans* mixture) by reduction of crotonaldehyde with aluminium isopropylate⁷. All the substrates were distilled before use and they were chromatographically pure. Of the original series of nineteen solvents employed in the preceding work¹, cyclohexane, diethyl ether, toluene, methanol, benzene, ethyl acetate and 1,4-dioxane were selected. Their purification as well as purification of hydrogen were described in the preceding work¹. All the solvents were chromatographically pure.

Apparatus and working procedure. The apparatus and working procedure were described earlier¹⁻³. The hydrogenation was performed in an agitated reactor at 20°C and atmospheric pressure of hydrogen. Hydrogenations were being made either with 1 ml of individual substrate or with 2—4 ml of the equimolar mixture of two substrates, always in 25 ml of the solvent; the amount of the catalyst varied from 0.1 to 0.2 g according to absolute rates of hydrogenation in separate solvents. Samples for chromatographic analysis of the volume of 0.1 ml were withdrawn during the proceeding reaction at appropriate time intervals. Volumetrically determined individual rates were corrected to the hydrogen partial pressure of 98 k Pa (760 Torr) and to the solvent vapour pressure assuming a first order reaction with respect to the hydrogen concentration¹. From measurements of competitive hydrogenations, the linear dependence $\log(c_i/c_i^0)$ versus $\log(c_j/c_j^0)$ was constructed with its slope given by the relation^{8,9}

$$S_{i,j} = (k_i/k_j) K_{i,j}. \quad (3)$$

By substituting values of reaction rates measured in the region of the zeroth order with respect to the substrate concentration for values k_i and k_j , values of relative adsorption coefficients were calculated from Eq. (3).

Analytical. Chromatographic analyses of reaction mixtures were performed on a Chrom-2 apparatus with flame-ionization detection. As the separation of mixtures of different substrates resulting from competitive hydrogenations in different solvents is too complicated, several chromatographic columns had to be used and many different conditions for individual determinations had to be tried. The analyses were performed at temperatures of 50—105°C, and the feed of sample was 1 μ l. The length of columns employed was 2.5—4 m, I.D. 2.5 mm, packings: 10% β, β' -oxydipropionitrile on Chromaton N-AW-HMDS, 20% polyethylene glycol 600 on Chezasorb, 10% polyethylene glycol 3000 on Chromaton N-AW, 15% silicone SF 96 on Chromaton N-AW-HMDS and 5% Reoplex 400 on Chromaton N-AW, mesh size 0.16—0.20 mm.

Evaluation of chromatograms was made on the assumption of equal relative molar responses of the saturated and unsaturated substance with the same skeleton.

RESULTS AND DISCUSSION

Kinetic measurements were performed at conditions where the reaction rate could not be affected by mass transfer^{1,3}. Values of reaction rates of the hydrogenated substrates in seven solvents in the region of the zeroth order with respect to the substrate concentration and recalculated to an unit amount of catalyst and the hydrogen partial pressure of 98 k Pa (760 Torr) are given in Table I. Some qualitative conclusions may be inferred from the measured data. In most solvents the hydrogenation proceeds with highest rates for 1-hexene and 3-butene-1-ol, highest hydrogenation

rates of separate substrates were observed usually in toluene and methanol, the lowest rates were found in benzene and 1,4-dioxane.

Structural relations manifested themselves *e.g.* in the hydrogenation of 2-butene-1-ol and 3-butene-2-ol, *i.e.* substances which have their —OH groups in the α -position with respect to the double bond, where the orders of solvents (except for toluene) with respect to decreasing hydrogenation rates were identical and similarly for 3-butene-1-ol and 1-heptene-4-ol, which have their —OH groups in the β -position to the

TABLE I
Hydrogenation Rates (r_n) of Model Compounds in Solvents Used

Substrate	2 ^a	4	10	11	12	13	15
A 1-hexene	41.65	102.00	102.20	96.90	11.40	79.50	12.10
B ethyl acrylate	24.40	45.20	55.10	40.30	15.95	23.35	27.80
C allyl phenyl ether	32.45	23.95	73.10	82.20	16.85	55.60	1.98
D allylbenzene	13.18	42.40	52.60	81.25	14.85	57.95	1.80
E 3-butene-1-ol	50.05	71.90	77.60	147.80	38.80	76.20	31.00
F 2-butene-1-ol	31.50	50.90	56.90	48.80	8.68	36.30	3.89
G 3-butene-2-ol	30.60	89.20	30.25	65.80	13.10	57.70	5.12
H 2-methyl-2-propene-1-ol	26.50	22.15	46.60	30.10	11.52	41.70	3.76
I 1-heptene-4-ol	29.52	34.80	59.00	49.60	15.10	68.00	4.10

^a Numbers of solvents agree with those from papers¹⁻³: 2 cyclohexane, 4 diethyl ether, 10 toluene, 11 methanol, 12 benzene, 13 ethyl acetate, 15 1,4-dioxane.

TABLE II
Results of the Regression Analysis; Correlations between Reaction Rates and Parameters τ' of the Set of Five Solvents

Substrate	λ'	q	α	$r_{x,y}$
A 1-hexene	2.46	—0.03	1.1	0.96
B ethyl acrylate	0.29	0.09	23.1	0.34
C allyl phenyl ether	3.71	—0.19	35.4	0.90
D allylbenzene	4.30	—0.16	30.8	0.99
E 3-butene-1-ol	1.39	—0.22	39.6	0.86
F 2-butene-1-ol	2.79	—0.01	2.3	0.92
G 3-butene-2-ol	3.10	0.02	4.7	0.96
H 2-methyl-2-propene-1-ol	2.42	0.04	9.6	0.90
I 1-heptene-4-ol	2.97	0.02	4.8	0.96

double bond, where these orders were identical with the exception of ethyl acetate and methanol.

In applying Eq. (1) to the given data set, the linear relation has not been confirmed unambiguously for any substrate. Benzene and toluene were falling out from all correlations as it is obvious *e.g.* from Fig. 1. After discarding these points, relation (1) resp. (4) became satisfied well for the remaining set of five solvents except for ethylacrylate (Table II). The critical value of the correlation coefficient was equal to 0.81 in the given case.

In evaluating parameter λ' by the regression analysis, the magnitude of the absolute term is given by q . According to definition Eq. (1), absolute term q in Eq. (4) should equal zero

$$\log r_a = (\log r_0 + q) + \lambda'\tau' \quad (4)$$

The value of q defined in this manner is the difference between the logarithms of the hydrogenation rate in methanol calculated according to Eq. (1) and the actual rate in methanol. The value of α expresses percentually the absolute difference between the experimental and calculated reaction rate in methanol related to the experimental rate in methanol. The absolute term is probably of no physical meaning. As experimental error is projected also into this term, it may serve to a certain extent, besides

TABLE III

Relative Adsorption Coefficients of Individual Substrates Related to 1-Hexene

$K_{i,j}$	Solvent ^a						
	2	4	10	11	12	13	15
$K_{B,A}^b$	11.15	3.46	3.97	4.28	1.95	4.72	1.25
$K_{C,A}$	3.29	20.01	3.32	4.64	0.53	3.83	1.75
$K_{D,A}$	3.38	6.51	4.12	3.23	0.47	2.60	1.80
$K_{E,A}$	41.60	6.17	21.95	1.01	0.92	4.01	1.89
$K_{F,A}$	6.60	1.18	4.86	0.52	3.56	1.57	2.96
$K_{G,A}$	19.40	5.45	40.10	2.21	8.05	6.12	5.74
$K_{H,A}$	12.10	2.95	15.90	1.02	6.70	1.77	4.56
$K_{I,A}$	11.40	3.12	14.40	1.11	5.77	1.29	1.15
$K_{P,A}^c$	41.10	14.00	— ^d	17.90	394	70.90	23.80
$K_{Q,A}^c$	2.54	1.36	5.88	0.42	5.78	0.74	0.28

^a Numbers for separate solvents agree with those in Table I. ^b Notation of substrates agrees with that in Table I. ^c Taken from paper³: P = 2-propene-1-ol, Q = 2-methyl-3-butene-2-ol.

^d Very high value.

the main criterion $r_{x,y}$, as a test of adequacy of using relation (1) for given systems. It follows from Table II that the value of parameter λ' depends on the structure of the hydrogenated substance. The highest sensitivity of the change in the reaction rate to the nature of the solvent is exhibited by substrate containing the benzene ring, a lower one by unsaturated alcohols and olefins. Ten values of λ' for unsaturated alcohols decrease in the order: secondary alcohol with monosubstituted double bond and with the —OH group in the α -position > secondary alcohol with monosubstituted double bond with the —OH group in the β -position > primary alcohol with bisubstituted double bond > primary alcohol with monosubstituted double bond. The value of parameter λ' for 1-hexene differs considerably from that established¹ for the original scale of nineteen solvents. This difference in both values might be due either to reduction of the solvent scale (Fig. 1) or to the absolute term in the testing equation; less probably it is a consequence of using two different batches of the catalyst in both cases. These results show that for the time being it is necessary to compare only consistent data.

The values of the relative adsorption coefficients of separate substrates were measured by the method of competitive reactions. As the direct measurements yielded relative adsorption coefficients of different substrate pairs selected with respect to possibilities of chromatographic analysis, some adsorption coefficients related to 1-hexene were obtained by recalculation from other measurements ($K_{B,D}$, $K_{C,D}$, $K_{H,1}$). Such

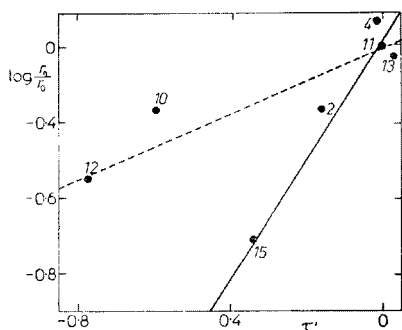


FIG. 1

Correlation between the Relative Rates of Hydrogenation of 3-Butene-2-ol in the Given Solvents and the Parameters τ'

The points for separate solvents are denoted by numbers which agree with those in Table I; solid line correlation with points 10 and 12 excluded, dashed line correlation for the entire set.

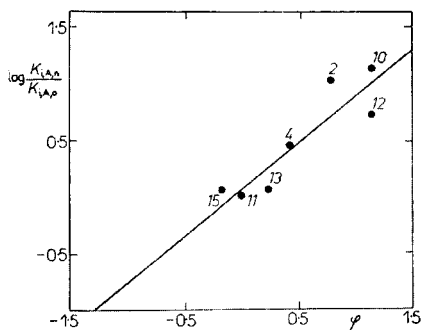


Fig. 2

Correlation between Relative Adsorption Coefficients of 1-Heptene-4-ol and 1-Hexene in the Given Solvents and the Parameters φ

The numbers at points for separate solvents agree with those from Table I.

recalculation is justifiable in cases where no disturbing interaction of both substrates occurs, which was confirmed³ *e.g.* for a 2-propene-1-ol, 2-methyl-3-butene-2-ol and 1-hexene system. The results are in Table III. Among other things an interesting relation between adsorptivities of 1-hexene and unsaturated alcohols follows from this table. Sorption of olefins or unsaturated alcohols is preferred in polar or nonpolar solvents, resp. Adsorptivity of unsaturated alcohols is affected by positions of the double bond and —OH group; it decreases with increasing degree of substitution of the double bond, with increasing distance between the —OH group and the double bond and with increasing degree of substitution of carbon which binds the —OH group. Eq. (2) resp. (5) was applied to the given data set. Results of the regression analysis are in Table IV. The critical value of the correlation coefficient is equal to 0.67. Absolute term q is defined by the equation

$$\log K_{i,j,n} = (\log K_{i,j,0} + q) + \gamma\varphi \quad (5)$$

and its meaning, similarly to the meaning of parameter α , is analogous as in the case of Eq. (4) (Table II). An example of the correlation of relative adsorption coefficients by Eq. (5) is in Fig. 2. Successful correlations were obtained only for unsaturated alcohol-unsaturated hydrocarbon systems, *i.e.* for systems analogous to the standard system selected for determining values of φ . The validity of proposed relations (2) resp. (5) will be therefore limited to such systems, however, it is not excluded that an analogous approach would be successful also for other systems with similar substances. No system has been found so far for which the change in the relative adsorptivity with the change in the solvent would be so significant as for the

TABLE IV

Results of the Regression Analysis: Correlation between Relative Adsorption Coefficients and Parameters φ of the Set of Seven Solvents

$K_{i,A}$ i	γ	q	α	$r_{x,y}$
B ^a	0.14	—0.15	29.2	0.25
C	—0.28	—0.02	4.3	—0.31
D	—0.16	—0.02	4.6	—0.23
E	0.51	0.40	151.5	0.42
F	0.46	0.41	157.5	0.63
G	0.58	0.28	90.5	0.75
H	0.61	0.33	113.7	0.74
I	0.82	0.11	28.8	0.91

^a Notation of substrates agrees with that in Table I.

TABLE V
Values of Polar and Steric Parameters of Substituents Used

Substituent	σ^*	E_s^a
—CH ₃	0.00	0.00
—CH ₂ C ₆ H ₅	0.225	—0.38
—CH ₂ OC ₆ H ₅	0.85	—0.33
—H	0.49	1.24
—COOC ₂ H ₅	0.89	—
—CH ₂ OH	0.55	0.03 ^b
—C ₄ H ₉	—0.13	—0.39
—CH(OH)CH ₃	—	0.09 ^b

^a Values of E_s include the hyperconjugation effect. ^b Ref. ¹², the rest from ref. ¹¹.

pair unsaturated alcohol–unsaturated hydrocarbon. In all cases of successful correlations, a relatively high value of constant q and consequently a high value of α were established. The introduction of parameter q is obviously far better substantiated than in the case of Eq. (4) whereas its physical meaning remains still vague. It is possible that it compensates another solvent parameter which is not included in parameter φ .

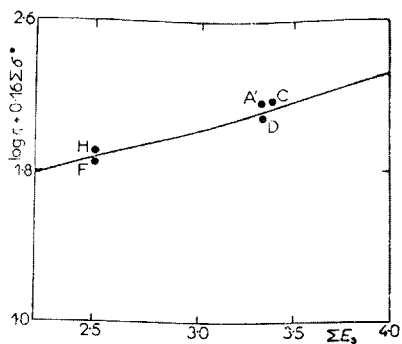


FIG. 3

Correlation between Hydrogenation Rates of Olefinic Substrates in Ethyl Acetate and Polar and Steric Parameters of Substituents

The letters denote individual substrates in agreement with Table I.

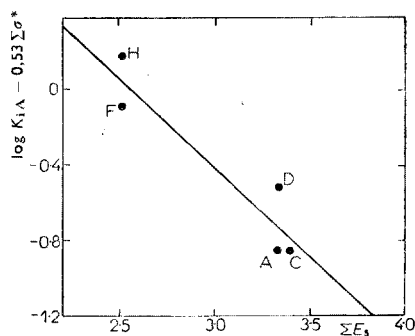


Fig. 4

Correlation between Adsorption Coefficients Related to 1-Hexene for the Hydrogenation in Cyclohexane and Polar and Steric Parameters of Substituents

The letters denote individual substrates in agreement with Table I.

If points with largest derivations from correlations are discarded ($K_{E,A}$ – point 12, $K_{F,A}$ – point 15, $K_{H,A}$ – point 15), to small exceptions we obtain an opposite trend for these corrected values of γ for separate substrates than for values of λ' . This is an interesting finding with respect to the fact that definition equations (1) and (2) do not take into account any relation between these parameters; thus it points to a connection between the effects of the structure of substrate and the reaction medium on the reaction rate and adsorptivity of given substances.

For evaluation of the effect of the structure of substrates on the hydrogenation rate and adsorptivity in given solvents, Taft's equation¹⁰ had been chosen. Values of polar and steric parameters of selected substituents, which were taken from the literature^{11,12}, are given in Table V. These values are not available for the remaining substituents employed. The following relations were used for the testing

$$\log r_{i,n} = \varrho_r^* \sum_1^4 \sigma^* + \delta_r \sum_1^4 E_s + x, \quad (6)$$

$$\log (K_i/K_A)_n = \varrho_a^* \sum_1^4 \sigma^* + \delta_a \sum_1^4 E_s + y. \quad (7)$$

For the reaction centre of individual model substances, the isolated double bond C=C was taken and the summation of polar resp. steric constants of individual substituents was performed. It is obvious that x is an apparent value of $\log r_{i,n}$ and y of $\log (K_i/K_A)_n$, where i stands for 2,3-dimethyl-2-butene with its double bond fully substituted by methyl groups.

The correlations were performed for all solvents and five substrates (A, C, D, F, H) for which values of σ^* and E_s were available for all substituents. The correlation coefficient of the linear dependence of values $\sum \sigma^*$ and $\sum E_s$ is low ($r_{x,y} = 0.53$)

TABLE VII

Results of the Regression Analysis; Correlation between Relative Adsorption Coefficients and Polar and Steric Parameters according to Eq. (6)

Solvent	ϱ_a^*	δ_a	y	$r_{x,y,z}$	s	$r_{x,y}$	$r_{x,z}$
2	0.53	-0.94	2.40	0.82	0.23	-0.04	-0.80
4	0.51	-0.89	2.29	0.57	0.35	-0.02	0.71
10	1.27	-0.02	-1.86	0.85	0.28	0.93	0.47
11	0.61	0.37	-2.11	0.84	0.21	0.85	0.76
12	-0.18	-0.98	3.45	0.92	0.19	-0.60	-0.96
13	0.57	-0.11	-0.48	0.85	0.12	0.90	0.31
15	0.26	-0.58	1.58	0.85	0.13	-0.16	-0.86

TABLE VI

Results of the Regression Analysis: Correlation between Reaction Rates and Polar and Steric Effects according to Eq. (5)

Solvent	ϱ_r^*	δ_r	x	$r_{x,y,z}$	s	$r_{x,y}$	$r_{x,z}$
2	-0.02	-0.04	1.59	0.98	0.27	-0.09	-0.12
4	-0.64	0.45	1.52	0.67	0.20	-0.55	0.26
10	-0.12	0.23	1.33	0.25	0.14	0.06	0.61
11	-0.09	0.46	0.59	0.86	0.10	0.35	0.92
12	0.16	0.11	0.44	0.79	0.07	0.81	0.76
13	-0.16	0.32	1.07	0.92	0.05	0.09	0.86
15	-0.72	0.27	1.17	0.36	0.31	-0.68	-0.91

so that the selected series is satisfactory also from the point of view of possible differentiation between polar and steric effects.

Correlation of the measured data by Eq. (6) or (7) was successful for cyclohexane, methanol, benzene and ethylacetate (Table VI) or for all solvents except for diethyl ether (c. Table VII), resp. Figs 3 and 4 are examples of successful correlations. The substrate may be bonded to the catalyst not only through its double bond but also through other "substituents". From case to case it leads to a change in the amount of active centres available for the hydrogenation. Besides this, disturbing interactions between solvent and hydrogenated substrates might also come into effect. These effects may result in failing of the correlations whereas a more precise interpretation is not possible for the time being because of scarcity of experimental data. Negative values of parameter ϱ_r^* and positive ones for δ_r were established for most correlations of reaction rates with polar and steric parameters (Eq. (6)), correlations of relative adsorption coefficients (Eq. (7)) yielded opposite results. The observed opposite values of the reaction ϱ_r^* and adsorption ϱ_a^* parameter are interesting from the point of view of work¹³, where positive values of ϱ_r^* and negative ones for ϱ_a^* were established for hydrogenation of alkyl ketones.

This interesting compensation of the kinetic and adsorption parameter occurs in the kinetics of heterogeneously catalyzed reactions also in other cases, *e.g.* for the dependence of the rate constant and adsorption coefficient in the Langmuir-Hinshelwood equations on the strength of acidity of the catalyst¹⁴, or in the case of the above mentioned opposite trend of values of λ' and γ , and its validity is obviously more general.

Besides values of ϱ^* and δ , Tables VI and VII contain values of correlation coefficients obtained by the method of double linear regression ($r_{x,y,z}$), values of standard deviation (s) and correlation coefficients of simple linear regressions (dependence

of $\log r$ resp. $\log K_{i,A}$ on $\sigma^*(r_{x,y})$ resp. $E_s(r_{x,z})$. In the given set of hydrogenated substances were both the reaction rate and relative adsorptivity of substrates in most solvents affected to a comparable extent by steric and polar effects as it is obvious from Table VI.

Our work thus confirmed the possibility of quantitative description of the effects of solvents and structure of olefinic substrates on the rate of catalytic hydrogenation and on the relative adsorptivity of hydrogenated substrates. A further generalization of the derived relations is limited by scarcity of necessary experimental data.

Thanks are due to Mr J. Bartoň for his statistical evaluation of our experimental data.

LIST OF SYMBOLS

c	concentration (mol/l)
E_s	value in Eq. (6) expressing the steric effect of substituent
k	rate constant (dimension according to the form of the kinetic equation)
$K_{i,j}$	relative adsorption coefficient of substances i and j
q	absolute term in Eq. (4) resp. (5)
r	rate of hydrogenation ($\text{ml H}_2 \cdot \text{min.}^{-1} \text{ g}_{\text{cat}}^{-1}$)
$r_{x,y}$	correlation coefficient of the simple linear dependence
$r_{x,y,z}$	correlation coefficient of the double linear dependence
s	standard deviation
S	selectivity factor defined in Eq. (3)
x	parameter defined in Eq. (6)
y	parameter defined in Eq. (7)
α	absolute value of the difference between the measured and calculated (Eq. (4)) reaction rate in methanol related to the measured rate in methanol (%)
γ	parameter in Eq. (2) characterizing the sensitivity of the change in relative adsorptivity to the change of solvent
ϕ	parameter in Eq. (2) characterizing the effect of solvent on the relative adsorption coefficient of two substrates
λ'	parameter in Eq. (1) characterizing the sensitivity of the change in the rate constant to the change of solvent
τ'	parameter in Eq. (1) characterizing the effect of solvent on the rate constant of hydrogenation
ρ^*	constant in Eq. (6) expressing the sensitivity to the change in polar influence
σ^*	constant in Eq. (6) expressing the polar effect of the substituent
δ	constant in Eq. (6) expressing the sensitivity to the change in the steric effect

Indexes

a	adsorption
i, j	general notation for substrates
n	n -th solvent
o	solvent taken for the basis of the correlation (methanol)
r	reaction

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