

EFFECT OF SOLVENT ON CATALYTIC HYDROGENATION OF 1-OCTINE

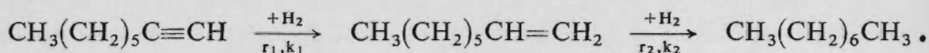
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Received November 11th, 1980

The effect of solvent on the course of the consecutive reactions in liquid phase was studied for hydrogenation of 1-octine on a platinum catalyst at 25°C using a series of 32 solvents. The reaction orders with respect to 1-octine, 1-octene, and hydrogen were determined by measuring the dependence of the initial reaction rates on the initial solute concentrations and on the partial pressure of hydrogen. The rate constants obtained for the hydrogenation stages were successfully correlated with the semiempirical parameters of the solvents.

The aim of the present work was to seek for a quantitative description of the solvent effect on the rates of hydrogenation of the two unsaturated compounds involved in the consecutive hydrogenation of 1-octine,



The solvent effect on the ratio of the 1-octine to 1-octene adsorption coefficients was also examined.

The effect of solvent on the rates of chemical reactions in homogeneous arrangement has been extensively studied. Various solvent parameters have been suggested for correlation with the rate and equilibrium constants. The most significant parameters are based on the assumption that the solvent is a homogeneous isotropic continuum surrounding the solute molecules. The intensity of the solvent-solute interaction then is determined by the macroscopic physical parameters of the former and the nature of the latter. The solvents effects are in this case referred to as nonspecific; they usually comprise the electrostatic, inductive, and dispersive effects whose intensity depends, on the one hand, on the static or induced charge distribution over the solute molecule, and on the other hand, on the macroscopic dielectric constant and polarizability (represented by the refractive index) of the solvent^{1,2}.

Parameters most widely used for expressing the nonspecific solvent-solute interactions are* the Scatchard function³ $1/D$, the Kirkwood function⁴ $K = (D - 1)/(2D + 1)$, the Onsager function⁵ $H = (n^2 - 1)/(n^2 + 2)$, and the Dimroth polarity parameter⁶ E_T expressing the effect of the solvent acidity.

Additional parameters have been suggested by David and Hallam⁷, $J = (D - 1)/(D - 2)$,

* See the appended list of symbols.

and by McRae⁸, $M = (n^2 - 1)/(2n^2 + 1)$ and $N = (D - 1)/(D + 2) - (n^2 - 1)/(n^2 + 2)$; Herbrandson and Neufeld⁹ have employed the Hildebrand parameter of the cohesive energy density, $\delta = (-e/v)^{1/2}$.

Other authors^{2,10} have suggested that use can be made of the linear free energy relationships to express various types of solvent-solute interaction through multiparameter correlation equations of the type

$$\Delta F_m - \Delta F_1 = \rho_A(A_m - A_1) + \rho_B(B_m - B_1) + \dots \quad (1)$$

The above parameters have not been so far applied to one- or multiparameter correlations of kinetic data derived from a heterogeneous catalytic reaction with a series of solvents.

EXPERIMENTAL

Chemicals. 1-Octene and 1-octene *p.a.* (both Koch-Light, Great Britain). All of the solvents were distilled with the catalyst prior to use to remove catalytic poisons which might be present. The catalyst was 5% platinum on Supersorbon Degussa activated carbon¹¹, grain size below 0.056 mm.

Apparatus and techniques. A standard apparatus was used involving an isothermal discontinuous reactor fitted with a rotary stirrer¹². The measurements were carried out at 25°C and atmospheric pressure. 0.05–0.2 g portions of the catalyst, 25 ml of the solvent, and 1 ml of 1-octene or 1-octene were used. The hydrogen take-up was monitored, and the reaction mixture was sampled for analysis in preselected time intervals. The reactions were conducted in the kinetic region, determined in the common fashion¹³.

Analysis. The samples were analyzed at 60–160°C on a Hewlett-Packard 7620A gas chromatograph equipped with a Minigrator Autolab digital integrator. The reaction mixtures were resolved into components on five stainless steel columns 3–7 m long, *i.d.* 2 mm, with packings as follows: 20% 1,2,3-tris-(cyanoethoxy)propane on Anakrom P (Analabs Inc.), 20% 1,2,3-tris-(cyanoethoxy)propane, 20% PEG 600, and 10% β,β' -oxydipropionitrile, all on Chromaton N-AW (Lachema, Brno), and 20% PEG 600 on Anakrom P.

RESULTS AND DISCUSSION

The reaction order with respect to hydrogen was determined from the experimental dependence of the hydrogenation rate of 1-octene in 2-propanol on the partial pressure of hydrogen. A drop in the latter could be achieved by rarefying the hydrogen stream with nitrogen in the semi-flow arrangement. The reaction order with respect to hydrogen was unity across the region of 25–101 kPa. The reaction orders with respect to 1-octene and 1-octene were determined from the dependences of the initial reaction rate on the initial concentrations of the substances; they were zero for both compounds at concentrations exceeding 0.1 mol l⁻¹. In view of the considerably higher adsorptivities of unsaturated compounds as compared with the solvents used¹³, the reaction order with respect to the substances was assumed to be zero also in the other solvents.

Taking into account the reaction orders found as well as the conclusions arrived at previously¹⁴ which have confirmed the independence of the adsorption coefficient of hydrogen (K_H) of the solvent used, the kinetic equation for the system under study can be written as

$$r = kK_H c_H = k' c_H. \quad (2)$$

Knowledge of the volume concentration of hydrogen in the solvent is prerequisite for the calculation of the kinetic constants based on this equation.

The rate constants were calculated from the initial reaction rates according to the relation

$$k' = r/\alpha_H \quad (3)$$

in which the volume concentration of hydrogen is replaced by Bunsen absorption coefficient.

The experimental time dependences of the component concentrations in the hydrogenation of 1-octene to octane *via* 1-octene obtained with the series of 32 solvents were processed on a Hewlett-Packard 9825A desk-top calculator by the nonlinear regression method¹⁵. The optimum polynomial functions fitting the kinetic curves were calculated (Fig. 1). Based on the maximum derivatives read off after the hydrodynamic equilibrium established at the beginning of the hydrogenation, the initial reaction rates were determined for the consumption or formation of the reactants or products, and from these, the corresponding rate constants were calculated according to Eq. (3). The maxima of the 1-octene concentrations ($c_{B,max}$) and the 1-octene concentrations corresponding to the maximum concentrations of the intermediate ($c_{A,max}$) were found on the curves and used to calculate the adsorption

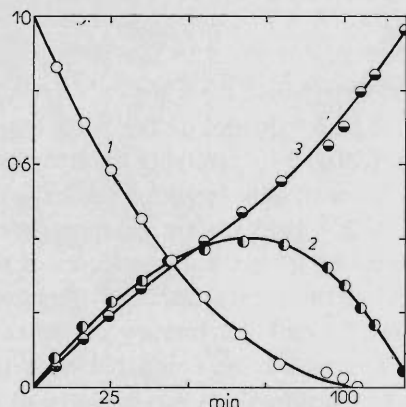


FIG. 1

Time dependence of the relative concentrations of the components involved in hydrogenation of 1-octene in benzene. 1 1-octene, 2 1-octene, 3 octane

coefficient ratio (K_A/K_B) according to the equation¹⁶

$$K_A/K_B = (k_2 c_{B,\max}) / (k_1 c_{A,\max}) \quad (4)$$

TABLE I

Rate constants of formation or take-up of the components in hydrogenation of 1-octene and 1-octene, selectivity and ratio of the adsorption constants of 1-octene and 1-octene

Solvent	k_1	k_2	k_3	k_4	$\frac{c_{B,\max}}{c_{A,\max}}$	k_1/k_2	K_A/K_B
Pentane	7.1	61.0	3.9	3.2	54	0.12	35.3
Hexane	13.6	57.1	9.1	6.3	5.0	0.24	21.0
Cyclohexane	22.8	109.1	10.2	12.5	4.6	0.21	21.5
Heptane	31.5	126.0	17.4	16.6	5.1	0.25	20.2
Diethyl ether	24.3	79.0	13.5	11.4	4.3	0.31	13.9
Dibutyl ether	22.5	65.5	10.5	12.6	2.7	0.34	7.9
Tetrahydrofuran	20.7	123.5	11.6	9.4	1.0	0.17	6.0
Dioxane	13.1	40.2	6.2	7.5	0.84	0.33	2.6
Benzene	17.4	51.1	8.6	8.8	4.5	0.34	13.2
Toluene	13.1	50.3	5.8	9.0	3.8	0.26	14.7
Ethylbenzene	19.8	48.2	10.2	9.3	4.2	0.41	10.2
Methanol	53.3	267.1	27.1	25.2	2.2	0.20	11.0
Ethanol	46.2	262.0	24.7	22.6	2.2	0.18	12.5
1-Propanol	31.9	183.9	14.8	18.5	1.8	0.17	10.4
2-Propanol	46.5	256.5	23.3	23.7	2.4	0.18	13.2
1-Butanol	42.9	183.4	20.3	24.5	1.2	0.23	5.1
2-Methyl-1-propanol	49.1	152.8	30.4	26.0	2.0	0.32	6.2
2-Methyl-2-propanol	24.0	169.2	9.9	14.5	0.82	0.14	5.8
1-Pentanol	28.2	166.1	16.1	12.7	0.60	0.17	3.5
3-Methyl-1-butanol	43.7	143.3	23.7	23.7	1.20	0.30	3.9
2-Methyl-2-butanol	26.5	140.7	9.6	16.8	0.72	0.19	3.8
1-Hexanol	30.2	81.2	11.3	20.5	1.10	0.37	2.9
1-Octanol	18.5	63.2	7.2	12.7	0.94	0.29	3.2
Benzyl alcohol	31.9	162.8	17.2	14.6	1.4	0.20	7.1
Cyclohexanol	46.6	140.0	20.1	26.9	0.90	0.33	2.7
Ethyl acetate	19.8	66.7	10.3	9.7	1.9	0.30	6.4
Isobutyl acetate	26.7	88.0	11.2	15.4	1.6	0.30	5.3
1-Pentyl acetate	23.6	61.4	12.4	17.2	1.1	0.38	2.3
Diethyl malonate	15.2	45.7	6.9	8.5	1.4	0.33	4.2
Ethylbenzoate	26.5	91.3	10.4	16.1	1.1	0.29	3.8
Acetylacetone	44.6	149.1	19.7	24.9	1.3	0.30	4.3
1,1,2,2-Tetrachloroethane	23.8	11.8	9.5	15.4	0.92	0.21	4.3

The rate constants calculated from the initial reaction rates according to Eq. (3) for the series of 32 solvents are given in Table I along with the ratios of the maximum concentrations of 1-octene to the corresponding concentrations of 1-octine ($c_{B,\max}/c_{A,\max}$) and the adsorption coefficient ratios (K_A/K_B). The k_1 quantity is the rate constant of the 1-octine consumption (Fig. 1, curve 1); the rate constant of the conversion of 1-octene (k_2) was determined in hydrogenation of 1-octene itself. In addition to the k_1 and k_2 constants, representing the model of the consecutive reactions, the curves 2 and 3 of Fig. 1 afforded also the rate constants of formation of the fraction of 1-octene that immediately desorbed from the catalyst surface (k_3) and of the fraction of 1-octene that did not desorb and was consecutively hydrogenated (k_4).

If the surface phenomena (adsorption, surface reactions, and desorption) are considered as a single stage, the reaction scheme can be looked upon as a system of parallel-consecutive reactions. The rate constant k_1 divides then into the k_3 and k_4 constants. It is not easy to experimentally distinguish between the two schemes — those of the consecutive and of the parallel-consecutive reactions; the actual time dependences of the component concentrations at the very beginning of the reaction are difficult to determine. The principal obstacle is the fact that at the beginning the hydrodynamic and sorption equilibria are only establishing, and moreover, the experimental error is higher in this region.

The rate constants, adsorption constant ratios, and the $c_{B,\max}/c_{A,\max}$ and k_1/k_2 ratios were correlated with the mentioned semiempirical parameters of the solvents according to Eq. (1), in which the measure of the free energy change was represented by the logarithm of the quantity correlated relative to the value in a standard solvent.

To the correlation was in addition applied also the empirical parameter of solvent τ , determined for a standard hydrogenation of 1-octene on 5% Pt/C by choosing $\lambda = 1$ and τ (methanol) = 0, analogously as in the works¹⁷⁻²¹.

The method¹⁵ adapted to multiparameter linear regression analysis was employed for the one- and two-parameter correlations. The solvent parameters are listed in Table II.

The rate constants measured in saturated hydrocarbons departed from the correlations and were not included in the final processing. Probably, some other mechanism of solvent-soluble interactions operates in this case.

The results of the one-parameter and two-parameter correlations are given in Tables III and IV, respectively.

The relations for the correlation coefficients r_{xy} and their critical values at the significance levels γ were taken from ref.²². The relative sensitivities of the correlated quantity to the various parameters (α) were calculated according to¹⁰.

As is apparent, the rate constant correlations obtained are very good. In the one-parameter arrangement, the K and $1/D$ parameters suited best, the E_T and δ parameters afforded good correlations too. With the parameter H , on the other hand, the correlation was unsatisfactory.

The correlation was improved by applying the two-parameter approach, particularly in the case of the $J-H$ and $M-N$ pairs combining the effects of the dielectric

TABLE II

Bunsen absorption coefficient of hydrogen and the semiempirical and empirical parameters of the solvents

Solvent	α_H	$1/D$	E_T^a	H	J	K	M	N	δ^b	τ^e
Pentane	0.134 ^c	0.542	—	0.218	0.220	0.180	0.179	0.002	7.0	-1.263
Hexane	0.120 ^c	0.532	30.9	0.227	0.227	0.185	0.185	0.001	7.3	-1.199
Cyclohexane	0.100 ^d	0.494	31.2	0.255	0.254	0.203	0.203	-0.001	8.2	-0.132
Heptane	0.105 ^d	0.520	—	0.234	0.235	0.191	0.190	0.001	7.4	-0.538
Diethyl ether	0.115 ^d	0.231	34.6	0.215	0.526	0.345	0.177	0.311	7.4	-1.005
Dibutyl ether	0.085 ^d	0.324	33.4	0.241	0.410	0.291	0.194	0.169	7.6	-1.050
Tetrahydrofuran	0.083 ^c	0.132	37.4	0.245	0.687	0.407	0.197	0.442	9.3	-2.349
Dioxane	0.051 ^d	0.453	36.0	0.153	0.287	0.223	0.202	0.034	9.7	-1.567
Benzene	0.069 ^d	0.440	34.5	0.293	0.298	0.230	0.227	0.005	9.2	-1.035
Toluene	0.080 ^d	0.420	33.9	0.291	0.315	0.239	0.225	0.024	8.9	-1.038
Ethylbenzene	0.046 ^c	0.416	—	0.291	0.319	0.242	0.225	0.028	—	-1.080
Methanol	0.087 ^d	0.031	55.5	0.202	0.914	0.447	0.168	0.711	14.5	0.000
Ethanol	0.073 ^d	0.041	41.9	0.220	0.887	0.470	0.180	0.667	12.9	0.194
1-Propanol	0.069 ^d	0.049	50.7	0.234	0.866	0.464	0.189	0.632	12.0	-0.160
2-Propanol	0.074 ^d	0.050	48.6	0.229	0.863	0.463	0.186	0.634	11.5	0.173
1-Butanol	0.063 ^d	0.057	50.2	0.241	0.846	0.458	0.194	0.605	10.7	-0.162
2-Methyl-1-propanol	0.050 ^c	0.056	—	0.239	0.849	0.459	0.193	0.610	—	0.370
2-Methyl-2-propanol	0.071 ^c	0.080	43.9	0.234	0.793	0.442	0.190	0.558	10.5	-0.243
1-Pentanol	0.062 ^d	0.072	43.9	0.247	0.811	0.448	0.198	0.565	—	-2.272
3-Methyl-1-butanol	0.047 ^c	0.068	47.0	0.245	0.820	0.451	0.197	0.575	—	-0.409
2-Methyl-2-butanol	0.067 ^c	0.172	—	0.243	0.616	0.381	0.196	0.373	—	-0.427
1-Hexanol	0.055 ^d	0.075	4.88	0.252	0.804	0.446	0.201	0.552	—	-0.978
1-Octanol	0.051 ^d	0.097	48.3	0.257	0.757	0.431	0.205	0.500	—	-1.229
Benzyl alcohol	0.019 ^c	0.076	50.8	0.313	0.801	0.445	0.238	0.489	12.1	-1.653
Cyclohexanol	0.009 ^c	0.067	—	0.276	0.824	0.452	0.217	0.547	—	-0.432
Ethyl acetate	0.078 ^d	0.166	38.1	0.226	0.626	0.385	0.184	0.400	9.1	-1.173
Isobutyl acetate	0.074 ^c	0.189	—	0.236	0.588	0.370	0.191	0.353	—	-0.897
1-Pentyl acetate	0.037 ^c	0.211	—	0.244	0.556	0.357	0.196	0.312	—	-2.174
Diethyl malonate	0.041 ^c	0.127	—	0.250	0.696	0.410	0.200	0.446	—	-1.552
Ethylbenzoate	0.022 ^d	0.166	41.3	0.296	0.626	0.385	0.228	0.330	—	-0.860
Acetylacetone	0.039 ^c	0.043	—	0.267	0.882	0.469	0.211	0.615	—	-0.370
1,1,2,3-Tetrachloroethane	0.014 ^c	0.122	31.9	0.290	0.706	0.414	0.225	0.416	—	-0.657

^a Refs^{6,24}; ^b refs^{9,10}; ^c ref.¹⁴; ^d ref.²⁵; ^e values measured in this work for standard hydrogenation of 1-octene on a Pt catalyst. The other parameters were calculated based on the dielectric constants and refractive indices from ref.²⁶.

constant and of the refractive index. As indicated by the relative sensitivities, the former effect dominates. An improvement appeared with the other pairs too, which gives evidence that the rate constant values are governed simultaneously by several interaction mechanisms.

That the application of the empirical equation¹⁷ is justified is borne out by the very good correlations of the rate constants with the τ parameter.

TABLE III

Results of one-parameter correlations with the E_T , δ , K , H , $1/D$, and τ parameters

Parameter		Correlated quantity						
		k_1	k_2	k_3	k_4	$\frac{c_{B,\max}}{c_{A,\max}}$	k_1/k_2	$K_A K_B$
E_T	Q	0.042	0.055	0.039	0.043	-0.055	0.001	-0.057
	r_{xy}	0.789	0.738	0.691	0.794	-0.639	0.044	-0.670
	m	19	19	19	19	16	16	16
	γ	0.1	0.1	1	0.1	1	—	1
δ	Q	0.175	0.259	10.65	0.171	-0.299	-0.080	-0.219
	r_{xy}	0.776	0.810	0.721	0.780	-0.683	-0.432	-0.639
	m	14	14	14	14	13	13	13
	γ	0.1	0.1	1	0.1	1	—	2
K	Q	3.809	5.191	3.554	3.909	-6.173	0.064	-6.205
	r_{xy}	0.819	0.799	0.702	0.830	-0.881	0.022	-0.890
	m	28	28	28	28	26	26	26
	γ	0.1	0.1	0.1	0.1	0.1	—	0.1
H	Q	-4.268	-6.718	-5.538	-2.862	-3.593	2.238	-5.779
	r_{xy}	-0.206	-0.320	-0.339	-0.188	-0.134	0.204	-0.217
	m	28	28	28	28	26	26	26
	γ	—	—	—	—	—	—	—
$1/D$	Q	-2.240	-3.028	-2.062	-2.311	3.586	-0.060	3.627
	r_{xy}	-0.808	-0.783	-0.684	-0.824	0.883	-0.036	0.897
	m	28	28	28	28	26	26	26
	γ	0.1	0.1	0.1	0.1	0.1	—	0.1
τ	Q	0.648	1.000	0.670	0.615	-0.724	-0.281	-0.444
	r_{xy}	0.779	1.000	0.772	0.708	-0.282	-0.257	-0.297
	m	32	32	32	32	32	32	32
	γ	0.1	0.0	0.1	0.1	—	—	—

TABLE IV

Results of two-parameter correlations with parameter pairs E_T-K , E_T-H , $E_T-\delta$, $J-H$ and $M-N$

Parameter pair	Correlated quantity							
	k_1	k_2	k_3	k_4	$\frac{C_{B,\max}}{C_{A,\max}}$	k_1/k_2	K_A/K_B	
E_T-K	$q(E_T)$	0.021	0.107	0.026	0.017	0.012	0.010	0.002
	$q(K)$	2.238	4.084	1.389	2.791	-6.923	-0.906	-5.987
	$\alpha(E_T)$	57	38	73	47	-7	-75	-1
	$\alpha(K)$	43	62	27	53	107	175	101
	r_{xy}	0.842	0.828	0.712	0.869	0.905	0.232	0.879
	m	19	19	19	19	16	16	16
	γ	0.1	0.1	0.1	0.1	0.1	-	0.1
	γ	0.1	0.1	0.1	0.1	0.1	-	0.1
E_T-H	$q(E_T)$	0.040	0.053	0.036	0.043	-0.053	0.003	-0.056
	$q(H)$	-1.605	-2.951	-3.593	-0.254	-2.919	-2.264	-0.671
	$\alpha(E_T)$	87	83	74	98	183	16	111
	$\alpha(H)$	13	17	26	2	-83	84	-11
	r_{xy}	0.797	0.757	0.731	0.794	0.650	0.259	0.671
	m	19	10	19	19	16	16	16
	γ	0.1	0.1	0.1	0.1	1	-	1
	γ	0.1	0.1	0.1	0.1	1	-	1
$E_T-\delta$	$q(E_T)$	0.078	0.104	0.074	0.085	-0.070	0.012	-0.080
	$q(\delta)$	-0.124	-0.133	-0.122	-0.148	0.026	-0.110	0.132
	$\alpha(E_T)$	163	146	168	174	99	81	96
	$\alpha(\delta)$	-63	-46	-68	-74	1	19	4
	r_{xy}	0.914	0.917	0.864	0.923	0.755	0.422	0.728
	m	14	14	14	14	13	13	13
	γ	0.1	0.1	0.1	0.1	1	-	1
	γ	0.1	0.1	0.1	0.1	1	-	1
$J-H$	$q(J)$	1.587	2.151	1.462	1.653	-2.646	-0.018	-2.616
	$q(H)$	-0.906	-2.491	-2.664	0.387	-1.711	2.251	-3.920
	$\alpha(J)$	90	81	74	105	109	6	124
	$\alpha(H)$	10	19	26	-5	-9	94	-24
	r_{xy}	0.840	0.826	0.754	0.840	0.870	0.205	0.881
	m	28	28	28	28	26	26	26
	γ	0.1	0.1	0.1	0.1	0.1	-	0.1
	γ	0.1	0.1	0.1	0.1	0.1	-	0.1
$M-N$	$q(M)$	1.585	2.144	1.457	1.653	-2.644	-0.020	-2.611
	$q(N)$	1.000	-0.757	-2.059	3.251	-7.078	3.626	-10.616
	$\alpha(M)$	107	96	87	127	123	7	141
	$\alpha(N)$	-7	4	13	-27	-23	93	-41
	r_{xy}	0.840	0.837	0.755	0.840	0.871	0.209	0.883
	m	28	28	28	28	26	26	26
	γ	0.1	0.1	0.1	0.1	0.1	-	0.1
	γ	0.1	0.1	0.1	0.1	0.1	-	0.1

Very good correlations were obtained also for the selectivity factor ($c_{B,\max}/c_{A,\max}$) and the adsorption coefficient ratio (K_A/K_B). However, the values measured in methanol, ethanol, and 1- and 2-propanol as well as in dioxane and 1-pentyl acetate were inconsistent with the correlations and were therefore omitted from them in the final processing.

Of the solvent parameters, the $1/D$ and K quantities derived from the dielectric constant gave the best correlations. In the case of the parameter pairs, the best results were obtained with the E_T - K pair, in which, however, it was again the K parameter that dominated, as is apparent from the α_K value.

The rate constant ratio k_1/k_2 , on the other hand, did not correlate with any of the solvent parameters; moreover, as can be seen from Table I, its value is little sensitive to solvent replacement as compared with the adsorption coefficient ratio. Hence, the selectivity of the formation of 1-octene is governed by the solvent effect on the adsorption coefficients of the solutes involved (or on their ratio).

The results of this work indicate that the solvent affects the hydrogenation rates of 1-octene and 1-octene on a Pt catalyst in two manners, *viz. via* the effect on the surface concentration of hydrogen and *via* the effect on the rate constant value. A competitive adsorption of the solvent cannot play a role, as the reaction order with respect to the solute is zero.

The correlations of the rate constants with the $1/D$, K , E_T , and δ parameters show that the rate constants of the catalytic hydrogenation are affected by the solvent "polarity", expressed by means of the parameters discussed. The solvent probably influences by its dielectric properties the formation and decomposition of the activated complex during the surface reaction.

On the other hand, the solvent has a substantial effect upon the competitive adsorption of the various solutes (Table I). Still, the adsorption coefficients of 1-octene and 1-octene are so high that if a single substrate is hydrogenated, the Langmuir equations reduce to ones of zero order.

In the case of hydrogenation of 1-octene the adsorption coefficient ratio K_A/K_B was also dependent upon the dielectric properties of the solvent.

The mechanisms of the solvent effects on the hydrogenation rate and on the octene to 1-octene adsorption coefficient ratio are probably different, although the dielectric properties are involved in both of them. While the hydrogenation rate is affected by the relation between the dielectric properties of the solvent and the bond energies of the activated complex, the adsorption coefficient ratio (K_A/K_B) probably depends on the relative solubilities^{2,3} of 1-octene with respect to 1-octene in the various solvents. This implies that the relative solubility of 1-octene increases with decreasing dielectric constant (with the exception of lower alcohols). The higher solubility of 1-octene relative to 1-octene then brings about its easier desorption, which operates against its consecutive hydrogenation, whereby the selectivity of formation of 1-octene is increased.

The results of this work thus indicate that the solvent effect on the rate and selectivity of a catalytic hydrogenation might be predicted based on the knowledge of the physical properties, particularly the dielectric constant of the solvent.

LIST OF SYMBOLS

A, B	general designation of the solvent parameters
c_i	concentration of the i -th component
D	dielectric constant
E_T	Dimroth parameter of the solvent polarity
ΔF	free energy change or measure of a phenomenon dependent on the solvent
H	Onsager function of the refractive index
J	David-Hallam function of the dielectric constant
k	rate constant of reaction (min^{-1})
k'	rate constant involving the adsorption coefficient of hydrogen ($\text{l g}_{\text{cat}}^{-1} \text{min}^{-1}$)
K	Kirkwood function of the dielectric constant
K_i	adsorption coefficient defined by the ratio of the surface and bulk concentrations of i -th component ($\text{l g}_{\text{cat}}^{-1}$)
m	number of equations correlated
M	McRae function of the refractive index
n	refractive index
N	Mc Rae function of the dielectric constant and the refractive index
r	reaction rate ($\text{mol min}^{-1} \text{g}_{\text{cat}}^{-1}$)
r_{xy}	correlation coefficient
α	relative sensitivity of the quantity correlated to the solvent parameters
α_{H}	Bunsen absorption coefficient of hydrogen (ml ml^{-1})
γ	level of significance
δ	Hildebrand parameter of cohesive energy density
λ	sensitivity parameter in equation of ref. ¹⁷
q	regression coefficient with respect to parameter A
τ	parameter of the solvent in equation of ref. ¹⁷

Subscripts

A, B, C	reacting components
H	hydrogen
m	m -th solvent
max	maximum value
1	standard solvent

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Translated by P. Adámek.