The Effect of Solvents on the Rate of Catalytic Hydrogenation of 6-Ethyl-1,2,3,4-tetrahydro-anthracene-9,10-dione

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ABSTRACT: The rate of hydrogenation of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione was investigated at 313 K and 0.1 MPa in 20 solvents. A multiple linear regression was used to describe the solvent effect. The regression of the reaction rates was carried out using two five-parameter linear regression models: the Abraham–Kamlet–Taft (AKT) and the Koppel–Palm (KP) model. After the elimination of the insignificant terms from the regression models, it was found that the basic character of the solvent and its Hildebrand cohesion energy density were the most important attributes influencing the hydrogenation rate. The analysis of both models led to the same conclusion. The resultant simplified AKT model gave closer fitting in comparison to the KP model. The results could facilitate the solvent selection for the industrial process of hydrogen peroxide production by the anthraquinone method with respect to the kinetics of anthraquinone hydrogenation. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 240–252, 2008

INTRODUCTION

Solvent Effects in Catalytic Hydrogenations

One of the important factors that influence the reaction kinetics in the liquid phase is the solvent used. The heterogeneously catalyzed hydrogenation is a typical example of a complicated three- or four-phase reaction system strongly influenced by the chosen solvent. The complexity of the system is evident from the fact that the solvent effect on the hydrogenation has been so far evaluated stochastically. In the following text, some conclusions of several publications dealing with this problem are cited.

Specific attributes, which must be named in connection with the mechanism of the influence of the solvent on the kinetics of a heterogeneously catalyzed hydrogenation, were summed up by Rajadhyaksha and Karwa [1] into four points:

1. different solubility of hydrogen in the reaction mixture,
2. competitive adsorption of solvent molecules on the active sites of the catalyst,

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3. agglomeration of catalyst particles, and
4. nonbonding interactions between reactant or product molecules with the solvent.

By using an example of 2-nitrotoluene hydrogenation in the presence of a 2 wt% Pd/C catalyst, the authors proved that the predominant effect on the rate of hydrogenation is precisely the interaction between the substrate and the solvent. They used four alcohols, benzene, *n*-hexane, and cyclohexane as solvents. In the case of a positive interaction, the adsorption ability of the reactant on the catalyst active site decreased; meanwhile, in the case of a negative interaction the adsorption was favored. They chose the activity coefficient of the hydrogenated substrate as a suitable parameter to describe the solvent effect.

Lo and Paulaitis [2] used the activity coefficient estimated by the UNIFAC contribution method [3] for the quantification of the solvation effect. They relatively succeeded in finding the correlation between the previously published hydrogenation rates of acetone and cyclohexene in the presence of nickel catalysts and the activity coefficients.

Iwamoto et al. [4] proved that the hydrogen adsorption enthalpy in C_1–C_4 alcohols is constant (11.3 kJ mol^{-1}) in their studies on the hydrogenation of toluene using Raney nickel. However, the values of the activation energy varied in the range 30.5–44.0 kJ mol^{-1}. They failed to clarify the trends in the variations of the reaction rates. On the contrary, Beketaeva et al. [5] proved that the solvent does not only influence the mechanism but also the adsorption enthalpy of hydrogen on the catalysts‘ surface in the hydrogenation of 2-methylbut-3-yne-2-ol. The consequence of this was different reaction rates and selectivities of hydrogenation with respect to the chosen combination of catalyst–solvent. The catalysts used were different group VIIIB metal black. The chosen solvents were water, 0.1 M NaOH solution, 1 M H_2SO_4, 96% ethanol, and *n*-heptane. The different concentrations of water in solvents used by Beketaeva et al. [5] could be the main reason of different conclusions to those of Iwamoto et al. [4].

Červený et al. [6] hydrogenated 2-methylbut-3-en-2-ol in the presence of a 5-wt% Pt/SiO_2 and 5-wt% Pt/C. For the evaluation of the solvent effect, they used the Drougard–Decroocq [7] model. The regression model, which was originally designed for reactions in a homogeneous phase, was successful only after the inclusion of structurally similar solvents (e.g., the homologous series of alcohols).

Rautanen et al. [8] investigated the hydrogenation of toluene in cyclohexane, *n*-heptane, and 2,2,4-trimethylpentane in the presence of a Ni/Al_2O_3 catalyst. Because of the structurally similar solvents, the authors attributed the different reaction rates only to the different solubilities of hydrogen in the reaction mixture.

Accessible information on the influence of solvents on the kinetics of heterogeneously catalyzed hydrogenation shows that the rate of hydrogenation clearly depends on the combination of the solvent used, the structure of the hydrogenated substrate, and the type of catalyst [9]. The solubility of hydrogen in the reaction mixture plays an important role, but in structurally different solvents other effects may occur, especially the different substrate–solvent interaction. Furthermore, a more complex situation occurs in the competitive hydrogenations when the solvent aids the adsorption of one of the substrates on the catalyst active sites and thus speeding up its hydrogenation. Different solvents can then aid different substrates [10].

Solvent Effect Interpretation Using Linear Free Energy Relationships

Certain potential for the quantification of the solvent effect on the kinetics of hydrogenation can be explored through the methods commonly used for the description of the solvent effect on the kinetics of homogeneous reactions in the liquid phase. The technique of multiple linear regression derived on the basis of the principle of linear free energy relationships (LFER) reliably enables the evaluation of the solvent effect of different physicochemical phenomena. The principle is based on the distribution of the physicochemical properties of the solvent into individual, mutually independent contributions. The number of contributions is given by the number of independent variables of the model.

The widely and elaborately used model is the Abraham–Kamlet–Taft [11] (AKT) model in the form shown in Eq. (1).

$$XYZ = XYZ_0 + d \cdot \delta + s \cdot \pi^* + a \cdot \alpha + b \cdot \beta + h \cdot \delta_{\mathrm{H}}^2 \qquad (1)$$

The terms d, s, a, b, and h represent solvent independent parameters of the model. These parameters characterize a given process, and they indicate its sensitivity on the solvent properties. The quantity XYZ is a dependent variable; XYZ_0 is an intercept whose physical meaning is the standard state of the quantity XYZ. The rest of the quantities are independent variables characteristic of a given solvent: π^* represents the solvent polarity, α is the hydrogen bond donor ability, and β is hydrogen bond acceptor ability of the solvent. The quantity δ_{H}^2 is the Hildebrand cohesion energy density, and it is defined as the heat of evaporation of the solvent at 298 K per unit volume (Eq. (2)). The term $d \cdot \delta$ in the AKT model is the correction on polarizability, and parameter δ has a value of 0.5 for polyhalogenated solvents, 1.0 for aromatic solvents, and zero for all other solvents.

$$\delta_{\mathrm{H}}^2 = \frac{\Delta H_v^{298} - \mathrm{R}T}{V_m^{298}} \tag{2}$$

The second important model is the Koppel–Palm [12] (KP) model with a Makitra et al. [13] modification in the form shown in Eq. (3).

$$XYZ = A_0 + A_1 \cdot f(n_D) + A_2 \cdot f(\varepsilon) + A_3 \cdot E_T + A_4 \cdot B + A_5 \cdot \delta_{\mathrm{H}}^2 \tag{3}$$

In this model, A_1–A_5 are solvent independent parameters, A_0 is an intercept with the similar meaning to XYZ_0, and XYZ is a dependent variable. In the KP model, the independent variables are the refractive index function $f(n_D)$, dielectric constant function $f(\varepsilon)$, electrophilic solvation ability E_T, nucleophilic solvation ability B of the solvent, and its Hildebrand cohesion energy density δ_{H}^2. The refractive index function $f(n_D)$ and the dielectric constant function $f(\varepsilon)$ are usually expressed by the Kirwood functions (4) and (5), respectively.

$$f(n_D) = \frac{n_D^2 - 1}{n_D^2 + 2} \tag{4}$$

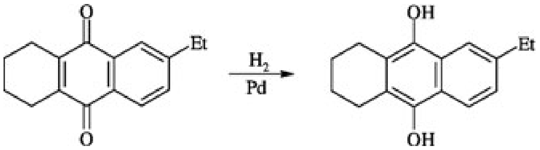
$$f(\varepsilon) = \frac{\varepsilon - 1}{2 \cdot \varepsilon + 1} \tag{5}$$

The given models have a wide application. In addition to the study of the solvent effect on the reaction rate, they could also be applied in the studies of the equilibrium constants in the liquid-phase reactions, the distribution coefficients between two liquid phases, the retention in gas chromatography, the solubilities of a given substrate in a solvent, the chemical shifts in nuclear magnetic resonance experiments, wavelength or wave number shifts in spectral characteristic measurements, the Gibbs energy, and the enthalpy values of equilibrium reactions.

Hydrogenation of 6-Ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione

The hydrogenation of anthraquinone derivatives is a typical example of a solvent-sensitive reaction. This reaction forms one step in the industrial production of hydrogen peroxide by the anthraquinone method. Chosen substrate 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione is in comparison with commercially more available structural analog 2-ethyl-9,10-anthraquinone significantly more resistant against deep hydrogenation and C—O bonds hydrogenolysis [14]. According to the patent literature, this process can be carried out using a wide range of solvent systems [15]. The selection criteria have so far been the physicochemical properties of the solvents. However, the comparison of the solvents in terms of their influence on the hydrogenation kinetics was usually neglected. Furthermore, the anthraquinone derivatives are particularly interesting for the study of solvation mechanisms in different solvents [16].

The objective of this work was to determine the reaction rate of the catalytic hydrogenation of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione (Eq. (6)) in the presence of a palladium-supported catalyst in some chosen solvents and the regression of experimental data using the AKT and KP models.



(6)

The main contribution of this work should be the description of the solvent effect on the kinetics of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione hydrogenation in a three-phase reaction system using the multiple linear regression models.

EXPERIMENTAL

Chemicals Used

Propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, pentan-1-ol, cyclohexanol, ethyl acetate, benzene, and 1,2-dichloroethane were supplied by Lachema (Brno, Czech Republic); cyclohexane, toluene and 1,4-dioxane were from Penta (Chrudim, Czech Republic); 2,2,2-trifluoroethanol, ethanol, *cis*-decaline, chlorobenzene, and triethylamine were from Sigma Aldrich; *m*-xylene was from Fluka Chemie GmbH; 2-methylpropan-2-ol was from former Koch-Light Laboratories Ltd. (Colnbrook, UK); 2-ethylanthracene-9,10-dione was delivered by BASF Aktiengesellschaft (Ludwigshafen, Germany); 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione was synthesized via a Dawsey et al. [17] procedure.

The chemicals were supplied with purity p.a. (analytical grade). The solvents were refined by distillation with sodium under nitrogen atmosphere and dried using a molecular sieve UOP type 3 A (Fluka) before application.

The hydrogenation catalyst was an MGS5-type of composition 2 wt% Pd/Al_2O_3-SiO_2 in powder form, supplied by Süd-Chemie MT S.r.l. Montecatini Technologie Catalysts (Novara, Italy).

Apparatus and Procedures

The hydrogenations were carried out in the presence of a palladium catalyst at 313 K and 0.1 MPa in a laboratory glass batch reactor (38 cm^3) equipped with a magnetic stirrer (4500 rpm). A combination of the chosen substrate, mild reaction conditions, and a low amount of the suitable catalyst enables to lead the hydrogenation with a 100% selectivity without respect to the chosen solvent. In order for the hydrogenation to take place in the kinetic regime even at high-reaction rates, the reactor was equipped with horizontal baffles that enabled higher mixing efficiency.

The kinetic region in terms of external mass diffusion was achieved by specific reactor construction and by intensive stirring of the reaction mixture. The reactor was equipped with eight fixed baffles in sets of four placed in two rows above each other. The baffles were in the shape of the Lorentz curve and had a circular cross section. The aerodynamic shape of the baffles ensured the elimination of an axial vortex and the adherence of the catalyst particles in inaccessible parts of the reactor. The verification of the kinetic region was carried out by the measurement of the hydrogenation rates as a function of the rotational speed of the impeller for cyclohexanol. The rate of hydrogenation was constant in the range between 3800 and 4500 rpm. Cyclohexanol was chosen because it had the lowest value of Reynolds number Re_M for mixing based on the initial hydrogenation rate [18].

The kinetic region in terms of internal mass diffusion using a catalyst with nonuniform palladium loading (catalyst MGS5) is impossible to verify by a standard procedure of catalyst particle sieving. Therefore, the internal mass-transfer limitations were considered empirically. In the hydrogenation of anthraquinone derivatives, the internal diffusion can only be limited by the mass transfer of hydrogen and not by the mass transfer of anthraquinone. This is caused by 10^5–10^6 times lower concentration of hydrogen compared to anthraquinone. The differences in concentration cannot be compensated by 10^1–10^2 times higher effective diffusion coefficient of hydrogen compared to anthraquinone. Thus, the kinetic region in terms of the internal diffusion was verified using the Weisz–Prater criterion Φs for hydrogen [19]. The Weisz–Prater criterion did not surpass its critical value of 0.3 even in the most viscous cyclohexanol.

The catalyst was activated in situ before the hydrogenation. Amounts of 10 mg of catalyst and 1 cm^3 of solvent were fed into the reactor, and the suspension was mixed in a hydrogen atmosphere for 30 min at reaction conditions. In this way, the catalyst was brought to a standard state in which its activity was constant during the course of hydrogenation. After the catalyst activation, 19 cm^3 of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione solution in a given solvent was fed into the reactor. The initial substrate concentration in the reaction mixture was 84 mmol dm^{-3}, and the total volume of the liquid phase was 20 cm^3. After filling the reactor with hydrogen, the reaction was initiated. The hydrogenation kinetics was monitored by measuring the time dependency of hydrogen consumption using a gas volumetric burette.

Computational Details

The actual reaction rate $r_{\xi,i}$ in the conversion range ξ for the solvent i was evaluated from the dependence of hydrogen moles consumed in time and per unit amount of catalyst. If the range is narrow enough, the experimental points in this interval can be described by linear regression with high-close fitting. The slope of the resultant line divided by the catalyst amount gives the actual hydrogenation rate for the corresponding conversion interval. The evaluation carried out using linear regression of the experimental points by the least-squares method. The so-called initial reaction rate $r_{0,i}$ was determined in the conversion range $\xi \equiv 3\%$–15%, the other actual rates were determined in the conversion ranges 20%–25% ($r_{20,i}$), 50%–55% ($r_{50,i}$), and 70%–75% ($r_{70,i}$).

The difference in hydrogen solubility in the reaction mixture with respect to various solvents used was eliminated by the introduction of the corrected actual reaction rate $r^c_{\xi,i}$ according to Eq. (7), where $x_{H_2,i}$ is the hydrogen mole fraction dissolved in the liquid phase.

$$r^c_{\xi,i} = \frac{r_{\xi,i}}{x_{H_2,i}} \tag{7}$$

The introduction of the corrected hydrogenation rate (Eq. (7)) assumes a first reaction order with respect to hydrogen in all chosen solvents. This assumption could experimentally be verified by the measurement of the hydrogenation rates at various pressures with simultaneous knowledge of the pressure dependence of hydrogen solubility. Such a dependence is not known for each solvent used. Hence, the first reaction order with respect to hydrogen was not experimentally verified but it was assumed in agreement with the results of Santacesaria et al. [20].

By experimental verification, the hydrogenation was carried out in the kinetic region with respect to external mass diffusion; hence, the equilibrium hydrogen concentration in the reaction mixture was guaranteed. The hydrogen concentration in the reaction mixture was considered negligible in the reactant and product solution; hence, it was taken as hydrogen solubility in a pure solvent.

Regression calculations were computed using the QC.Expert 2.7 software by the common least-squares method. All the diagnostic tests were determined at 95% significance level. The quantities used for this purpose were also computed using the QC.Expert software, and their definitions can be found, for example, in Meloun and Militky [21,22].

Tabulated Data Collection

It was necessary to collect a lot of tabulated values for successful regression calculations. The variables in AKT and KP models and hydrogen solubilities in pure solvents (see Table I) represent a series of physicochemical quantities that are available from various sources. The variables π^*, α, β, and $E_T(30)$ were taken from Marcus [23]. The Dimroth–Reichardt characteristic $E_T(30)$ was used to express the electrophilic solvation ability of the solvent in the KP model instead of the original E_T quantity. The nucleophilic solvation ability of solvent B for the interaction solvent–phenol was accepted (in some works this quantity is assigned B' to distinguish it from the original nucleophilicity quantifying the interaction solvent–methan(^{2}H)ol), and it was taken from Aslam et al. [24] (alcohols) and Abboud and Notario [25] (the rest of the solvents). The unavailable value B for 2,2,2-trifluoroethanol was obtained from the correlation between infrared stretching frequency shifts of the OH group for solvated 2,2,2-trifluoroethanol with corresponding shifts for solvated phenol published by Purcell and Wilson [26]. The variables $E_T(30)$ and B were normalized according to the expressions (8) and (9), respectively. To compute the normalized quantities for the ith solvent $E^N_{T,i}$ and B^N_i, the electrophilic solvation ability of water ($E_T(30)_{\mathrm{H_2O}} = 264$ kJ mol^{-1}), the electrophilic solvation ability of trimethylsilane ($E_T(30)_{\mathrm{TMS}} = 129$ kJ mol^{-1}), and the nucleophilic solvation ability of hexamethylphosphoric amide ($B_{\mathrm{HMPA}} = 471$ cm^{-1}) had to be known.

$$E^N_{T,i} = \frac{E_T(30)_i - E_T(30)_{\mathrm{TMS}}}{E_T(30)_{\mathrm{H_2O}} - E_T(30)_{\mathrm{TMS}}} \tag{8}$$

$$B^N_i = \frac{B_i}{B_{\mathrm{HMPA}}} \tag{9}$$

The variable δ^2_{H} presented in both models was calculated by the standard procedure according to (2) and expressed in kJ cm^{-3}. The enthalpies of vaporization ΔH^{298}_v required to calculate δ^2_{H} for most of the solvents were obtained from thermodynamic tables [27], and for 2,2,2 trifluoroethanol the enthalpy of vaporization was obtained from Rochester and Symonds [28]. The function of the refractive indices and the dielectric constants were calculated according to Kirkwood functions (4) and (5), respectively. Into the Kirkwood expressions, the tabulated [29] refractive index of yellow sodium line at 293.15 K and the static dielectric constant [30] of the solvent at either 298.15 K or at reaction temperature were inserted.

Hydrogen solubilities in various solvents were taken from the Battino et al. [31] tables. However, more contemporary data available for butan-1-ol [32], butan-2-ol [33], 2-methylpropan-1-ol [34], and 2,2,2-trifluoroethanol [35] were used. The inaccessible values for methylcyclohexane and triethylamine were obtained by approximation. The dependence of the hydrogen solubility for 11 other gases (He, Ne, Ar, Kr, N_2, O_2, CO, CO_2, CH_4, CF_4, SF_6) in methylcyclohexane on the hydrogen solubility of these gases in cyclohexane was found to be linear [36]. The dependence had high-close fitting with a correlation coefficient of 0.999. Thus, the hydrogen solubility in methylcyclohexane was computed by extrapolation from this dependence. The solubility of hydrogen in triethylamine was obtained from its pressure dependence [37].

RESULTS AND DISCUSSION

Preliminary Data Analysis

The hydrogenation of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione was carried out in 20 solvents. These included 10 alcohols (of which one was fluorinated), 4 aromatics, 2 saturated hydrocarbons, ether, ester, amine, and an alkylchloride. With a few solvents, it was impossible to determine the hydrogenation rate at some conversion intervals. This was due to the low solubility of the hydrogenation product in these solvents. The precipitation of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-diol was very fast and easily detectable by visual observation due to the transparent glass reactor. The conversion intervals in which the actual hydrogenation rates were determined were selectively chosen to eliminate the precipitation effect on the hydrogenation.

Table I Variables of the AKT and KP Models Used in the Regression and the Hydrogen Solubility

	Solvent	δ	π^*	α	β	$f(n_D)$	$f(\varepsilon)$	$f(\varepsilon')$	E_T^N	B^N	δ_{H}^2 (kJ mol^{-1})	x_{H_2} ($\times 10^4$)
1	2,2,2-Trifluoroethanol	0.0	0.73	1.51	0.00	0.19	0.47	0.47	0.90	0.23[a]	0.56	2.77[b]
2	Ethanol	0.0	0.54	0.86	0.75	0.22	0.47	0.47	0.65	0.49	0.68	2.06
3	Propan-1-ol	0.0	0.52	0.84	0.90	0.23	0.46	0.46	0.62	0.49	0.60	2.31
4	Propan-2-ol	0.0	0.48	0.76	0.84	0.23	0.46	0.46	0.57	0.51	0.56	2.66
5	Butan-1-ol	0.0	0.47	0.84	0.84	0.24	0.46	0.45	0.60	0.50	0.54	2.69[c]
6	Butan-2-ol	0.0	0.40	0.69	0.80	0.24	0.45	0.43	0.51	0.51	0.51	2.73[d]
7	2-Methylpropan-1-ol	0.0	0.40	0.79	0.84	0.24	0.46	0.45	0.55	0.49	0.52	2.88[e]
8	2-Methylpropan-2-ol	0.0	0.41	0.42	0.93	0.24	0.44	0.43	0.40	0.53	0.47	3.00
9	Pentan-1-ol	0.0	0.40	0.84	0.86	0.25	0.45	0.44	0.57	0.50	0.50	3.29
10	Cyclohexanol	0.0	0.45	0.66	0.84	0.28	0.45	0.45	0.50	0.52	0.56	1.68
11	1,4-Dioxane	0.0	0.55	0.00	0.37	0.25	0.22	0.22	0.16	0.50	0.42	1.76
12	Ethyl acetate	0.0	0.55	0.00	0.45	0.23	0.38	0.38	0.23	0.38	0.33	3.46
13	Methylcyclohexane	0.0	0.00	0.00	0.00	0.25	0.20	0.20	0.01	0.00	0.26	5.39[f]
14	*cis*-Decaline	0.0	0.11	0.00	0.08	0.28	0.22	0.22	0.02	0.00	0.31	3.61
15	Benzene	1.0	0.59	0.00	0.10	0.29	0.23	0.23	0.11	0.10	0.35	2.59
16	Toluene	1.0	0.54	0.00	0.11	0.29	0.24	0.24	0.10	0.12	0.33	3.15
17	*m*-Xylene	1.0	0.47	0.00	0.12	0.29	0.24	0.23	0.08	0.14	0.32	4.15
18	Chlorobenzene	1.0	0.71	0.00	0.07	0.31	0.38	0.37	0.19	0.08	0.38	2.65
19	1,2-Dichloroethane	0.5	0.81	0.00	0.10	0.27	0.43	0.42	0.33	0.08	0.41	1.78
20	Triethylamine	0.0	0.14	0.00	0.71	0.24	0.24	0.24	0.04	1.38	0.23	8.96[g]

ε: Static dielectric constant at 298 K.

ε': Static dielectric constant at a reaction temperature 313 K.

[a] Obtained by linear regression of the data published by Purcell and Wilson [26].

[b] Taken from the work of Mainar et al. [35].

[c,d,e] Taken from the works of Pardo et al. [32–34].

[f] Calculated as described in the text.

[g] Obtained from the dependence of hydrogen solubility on pressure published by Brunner [37].

The highest reaction rates were detected in most alcohols and in triethylamine. On the other hand, the lowest reaction rates were observed in methylcyclohexane, chlorobenzene, and 1,2-dichloroethane. In ethyl acetate, the hydrogenation rate was approximately one-third lower than the average rate in alcohols. In 2,2,2-trifluoroethanol, 1,4-dioxane, benzene, toluene, and *m*-xylene, the reaction rate was comparable (Table II).

The trends in the reaction rates cannot be described by any individual physical properties of the solvent. Therefore, to quantify the solvent effect on the hydrogenation, empirical linear expressions of solvation energy with the use of AKT and KP models were considered. To examine whether the variables of both models satisfy the condition of mutually independence, their partial correlation coefficients were investigated (Table III).

From Table III, the partial correlation coefficients explaining the variables showed strong mutual dependence in the α versus δ_{H}^2 pair of the AKT model and between the variables $f(\varepsilon)$ versus E_T^N, $f(\varepsilon)$, versus δ_{H}^2 and E_T^N versus δ_{H}^2 of the KP model. The partial correlation coefficient slightly exceeds its critical limit in several other combinations (Table III). A higher number of supercritical partial correlation coefficients and its larger values in most of the combinations signalized that the AKT model is designed better than the KP model.

To examine the extent of one-dimensional linear dependence of the measured reaction rates on individual variables of the AKT and KP models, the Pearson partial correlation coefficient is evaluated.

In Table IV, it is apparent that the strongest linear relationship exists between uncorrected initial hydrogenation rates and the hydrogen bond acceptor ability of solvent β. By correcting the concentration of hydrogen in the reaction mixture, the strength of this relationship decreased by 6% but at the same time the correlation with the Hildebrand cohesion energy density of the solvent increased by 28%. The dependence between the hydrogenation rate and the nucleophilic solvation ability of the solvent B^N of model KP is markedly weaker compared to the variable β, which has a similar meaning in the AKT model.

Table II Corrected Hydrogenation Rates of 6-Ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione with Respect to the Solvent Used at Four Different Conversions

	Solvent	$r^c_{0,i}$ (mol min^{-1} g$_{\text{cat}}{}^{-1}$)	$r^c_{20,i}$ (mol min^{-1} g$_{\text{cat}}{}^{-1}$)	$r^c_{50,i}$ (mol min^{-1} g$_{\text{cat}}{}^{-1}$)	$r^c_{70,i}$ (mol min^{-1} g$_{\text{cat}}{}^{-1}$)
1	2,2,2-Trifluoroethanol	17.4	13.8	Ins[a]	Ins
2	Ethanol	191.8	177.1	144.6	118.3
3	Propan-1-ol	153.7	143.6	126.9	111.2
4	Propan-2-ol	137.2	123.5	95.9	73.3
5	Butan-1-ol	131.4	115.4	99.5	87.4
6	Butan-2-ol	161.4	135.9	102.7	80.6
7	2-Methylpropan-1-ol	123.7	108.4	83.7	67.2
8	2-Methylpropan-2-ol	80.6	65.0	47.7	36.6
9	Pentan-1-ol	103.3	100.1	71.3	52.0
10	Cyclohexanol	146.0	129.1	96.7	74.2
11	1,4-Dioxane	24.5	19.9	13.5	<1.0
12	Ethyl acetate	33.6	25.9	25.1	16.3
13	Methylcyclohexane	0.3	Ins	Ins	Ins
14	*cis*-Decaline	9.5	3.8	Ins	Ins
15	Benzene	13.5	5.4	Ins	Ins
16	Toluene	16.1	7.3	Ins	Ins
17	*m*-Xylene	10.2	6.3	4.3	Ins
18	Chlorobenzene	7.2	6.4	3.2	2.8
19	1,2-Dichloroethane	4.6	3.0	<1.0	<1.0
20	Triethylamine	37.6	38.6	35.9	29.2

[a] Ins means that at a given conversion the hydrogenation product was insoluble in the reaction mixture; hence, it was impossible to determine the reaction rate.

Table III Partial Correlation of the Parameters in the Models AKT and KP

Paired variables	δ–π^*	δ–α	δ–β	δ–δ^2_{H}	π^*–α	π^*–β	π^*–δ^2_{H}	α–β	α–δ^2_{H}	β–δ^2_{H}
Partial correlation coefficient	0.402	**−0.510**	**−0.595**	−0.411	0.202	−0.146	0.397	**0.503**	**0.856**	**0.602**
Paired variables	$f(n_D)$–$f(\varepsilon)$	$f(n_D)$–E^N_T	$f(n_D)$–B^N	$f(n_D)$–δ^2_{H}	$f(\varepsilon)$–E^N_T	$f(\varepsilon)$–B^N	$f(\varepsilon)$–δ^2_{H}	E^N_T–B^N	E^N_T–δ^2_{H}	B^N–δ^2_{H}
Partial correlation coefficient	**−0.576**	**−0.709**	−0.431	**−0.538**	**0.909**	0.209	**0.856**	0.204	**0.921**	0.156

Partial correlation coefficients exceeding their critical limit at a significance level 95% are shown in bold.

Table IV Correlation of the Initial Hydrogenation Rates and the Individual Variables of the AKT and KP models

Expression of the Reaction Rate	$r_{0,i}$					$r^c_{0,i}$				
Variable of the AKT model	δ	π^*	α	β	δ^2_{H}	δ	π^*	α	β	δ^2_{H}
Pearson correlation coefficient	**−0.558**	−0.177	**0.595**	**0.926**	**0.623**	**−0.517**	−0.016	**0.667**	**0.868**	**0.823**
Variable of the KP model	$f(n_D)$	$f(\varepsilon)$	E^N_T	B^N	δ^2_{H}	$f(n_D)$	$f(\varepsilon)$	E^N_T	B^N	δ^2_{H}
Pearson correlation coefficient	−0.496	**0.620**	**0.589**	**0.694**	**0.623**	−0.438	**0.715**	**0.694**	**0.447**	**0.823**

The Pearson correlation coefficients exceeding their critical limit at a significance level 95% are shown in bold.

The Kirkwood function of dielectric constants and the reaction rate were strongly bound by a linear relationship, but a linear dependence of the polarity characteristic π^* and the reaction rate should not be expected. The rest of the values of the Pearson correlation coefficients ranged from ±0.5 to ±0.7. An entirely different result of the pairs correlation reaction rate versus $f(\varepsilon)$ and reaction rate versus π^* shows that the AKT and

KP models significantly differ to their approach of the effect of solvent polarity.

Precise Models Construction

The initial hydrogenation rate, which represents the dependent variable in the regression models, was expressed in two ways: the initial rate (uncorrected) and the initial rate corrected on the hydrogen solubility. The correlation coefficient increased from 0.949 to 0.972 for the AKT model and from 0.880 to 0.919 for the KP model after the correction. The closer fitting of the corrected rates called for a detailed discussion in the regression of these rates. The evaluation of the parameters XYZ_0, d, s, a, b, h, and A_0–A_5 is presented in Table V.

The determination of the statistical significance of the individual variables is possible using the calculated probability (p-level) that at 95% should not exceed a critical limit 0.05. In Table V, the critical limit of p-level was exceeded in the terms with the variables δ and α in the model AKT and in the terms with the variables $f(n_D)$, $f(\varepsilon)$, and E_T^N in the KP model. The α, $f(n_D)$, and $f(\varepsilon)$ variables were insignificant, and the terms in which they occurred were eliminated. The substitution of dielectric constant at hydrogenation temperature instead of the dielectric constant at 298 K caused the increase of the correlation coefficient by about 2% but had no effect on the significance of the term.

It is necessary to view the statistical significance of the variables in Table V with respect to partial Pearson correlation coefficients in Table IV. Although the p-level surpassed its critical limit by 3%–4% for the delta and E_T^N variables, these variables at the same time do not significantly correlate with the rest of the variables. The p-level was exceeded by 13%, 83%, and 19%, respectively, for the α, $f(\varepsilon)$, and $f(n_D)$ variables. However, these variables at the same time significantly correlate with the rest of the variables. Hence, the terms with the α, $f(\varepsilon)$, and $f(n_D)$ variables were found as statistically insignificant and they were eliminated from the models. After the elimination, simplified AKT and KP models with new regression parameters were obtained. The new p-levels did not exceed its critical limit. Even the significance of the regression parameters with delta and E_T^N decreased below its critical limit. The basic character of the solvent expressed by beta or B^N and the Hildebrand cohesive energy density δ_{H}^2 can be considered as the most significant properties influencing the hydrogenation kinetics. The Taft polarity/polarizability characteristics δ, π^*, and the Dimroth–Reichardt electrophilic ability E_T^N are also significant. Another way for the evaluation of statistical significance is the calculation of Mallows C_p values [38]. These are calculated for all of the potential models obtained by the elimination of a random number of random terms. In this way, the same results were obtained.

Models Comparison

The number of different tests and criteria have been used are standard in multiple linear regression fitting. They all are recommended and further explained in the works of Meloun and Militky [21,22].

Since the simplified models were now void of the insignificant terms, it was possible to compare the models in terms of their ability to describe the experimental data. In this respect, the mean square error of prediction (MEP) and the Akaike information criterion (AIC) were evaluated. By comparing the basic statistic quantities in the AKT model (10) and the KP model (11), it can be seen that the MEP value of the AKT model

Table V The Enumeration of the Regression Parameters in the Description of the Corrected Rates Using the AKT and the KP Models

	Model AKT					
	Intercept	d	s	a	b	h
Value of the regression parameter	−125.3	28.6	−112.9	−26.7	83.3	479.6
Standard deviation	24.0	15.6	32.6	19.1	17.2	89.2
p-level	0.000	0.088	0.004	0.183	0.000	0.000
	Model KP					
	Intercept	A_1	A_2	A_3	A_4	A_5
Value of the regression parameter	−231.4	62.0	191.8	−213.9	72.8	670.7
Standard deviation	105.1	407.8	161.0	112.3	25.4	158.0
p-level	0.045	0.881	0.235	0.078	0.012	0.000

Parameters h and A_5 are in $\mathrm{cm}^3\ \mathrm{kJ}^{-1}$, and other parameters are dimensionless.

is four times lower than MEP of the KP model and the AIC value of AKT model is about 13% lower than AIC of the KP model. Hence, both quantities indicate that the simplified AKT model is more suitable in terms of close fitting for the quantification of the solvent effect on corrected hydrogenation rates than the simplified KP model. On the other hand, according to the Scott criterion value, the simplified AKT model in contrast to the KP model showed a slight multicollinearity, which is caused by the stronger partial relationship of variables β versus δ_{H}^2 (Table II). The multicollinearity in the AKT model could be eliminated by the use of the generalized principal component regression method (GCPR) instead of the common least-squares method. However, this would decrease the accessibility of such a model. According to Fisher–Snedecor test, both simplified models were found to be significant. In other words, the corrected initial rate of hydrogenation is strongly dependent on the retained variables in the simplified models AKT and KP.

$$r_{0,i}^{c} = -103(\pm 18) + 34(\pm 16)\cdot\delta - 105(\pm 33)\cdot\pi^{*} + 90(\pm 17)\cdot\beta + 385(\pm 60)\cdot\delta_{\mathrm{H}}^{2}$$

$$R = 0.968,\ R_{\mathrm{adj}} = 0.780,\ \mathrm{MEP} = 479,\ \mathrm{AIC} = 121,\ F = 56.3 \tag{10}$$

$$r_{0,i}^{c} = -209(\pm 43) - 144(\pm 68)\cdot E_{T}^{N} + 77(\pm 22)\cdot B^{N} + 682(\pm 141)\cdot\delta_{\mathrm{H}}^{2}$$

$$R = 0.911,\ R_{\mathrm{adj}} = 0.282,\ \mathrm{MEP} = 1919,\ \mathrm{AIC} = 139,\ F = 25.9 \tag{11}$$

The other diagnostic tests were carried out for the residuals. Besides the identification of the influential points that are discussed below, no other important differences between the diagnostic tests of the AKT and the KP models were detected. From the Jarque–Berra test of residuals normality, it was found that the residuals have a Gauss distribution. From the Wald test, it was observed that the autocorrelation of the ordinary residuals is insignificant. And from the Cook–Weisberg test, the homoscedasticity was observed (constant residual distribution).

Influential Points Detection

A skilled identification of the outlying experimental points (outliers) for the multiple linear regression is a sophisticated problem that has been advanced in the last 20 years [22]. From Figs. 1 and 2, it cannot be easily distinguished which points are high-leverage points and which ones are the outliers. A number of diagnostic tools, which have been developed for this purpose, are able to indicate only the influential points and may not indicate the outliers [22]. However, a set of influential points is composed from a subset of outliers and a subset of high-leverage points (extremes). Some points could be incorporated in both subsets.

To detect the influential points, three types of diagnostic measures were used: diagnostics based on residual plots, diagnostics based on scalar influence measures, and diagnostics based on the diagonal elements of the hat matrix. Jackknife residuals are able to indicate the outliers. The diagonal elements of hat matrix are able to detect high-leverage points only. The Williams and McCulloh–Meeter plots can indicate both. The rest of the diagnostics used can detect influential points in general. The Pregibon plot is able to distinguish whether the point is strongly influential or intermediately influential.

Practically all the diagnostic tests showed the influential point for 2,2,2-trifluoroethanol in both models (see Table VI). The Williams plot and the jackknife residuals in the KP model indicated this point as outlier.

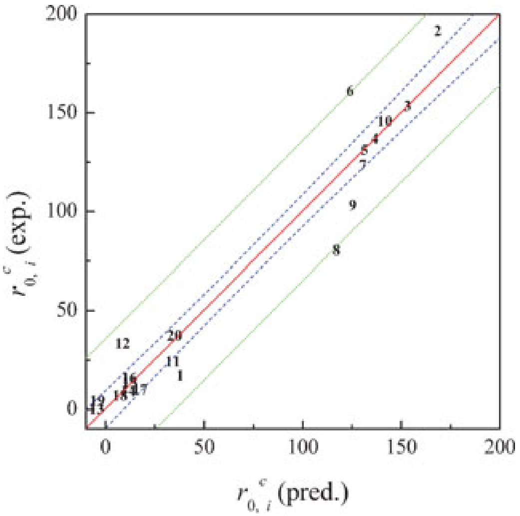


Figure 1 Dependence of the experimental values of corrected initial hydrogenation rates on the values predicted by the simplified AKT model; red (solid) line represents $y = x$ function, blue (dashed) lines represent the confidence bands, and green (dotted) lines represent prediction bands. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

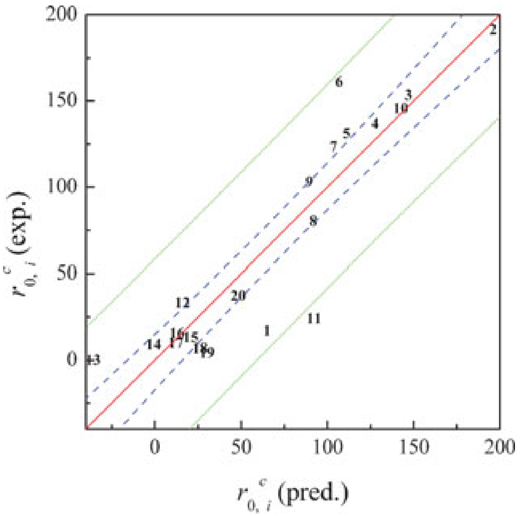


Figure 2 Dependence of the experimental values of corrected initial hydrogenation rates on the values predicted by the simplified KP model; red (solid) line represents $y = x$ function, blue (dashed) lines represent the confidence bands, and green (dotted) lines represent prediction bands. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The Williams plot, which appeared to be the most strictest of all diagnostics, indicated as outliers also butan-2-ol, 2-methylpropan-2-ol and ethyl acetate for the AKT model, and butan-2-ol and 1,4-dioxane for the KP model. The diagonal elements of Tukey's hat matrix showed high-leverage points for 2,2,2-trifluoroethanol and methylcyclohexane for the AKT model, and 2,2,2-trifluoroethanol, 1,4-dioxane and triethylamine for the KP model. The diagnostics, which are able to detect the high-leverage points only, were in agreement for the KP model, and they indicated 2,2,2-trifluoroethanol, 1,4-dioxane and triethylamine. For the AKT model, in addition to 2,2,2-trifluoroethanol, they indicated ethanol, 2-methylbutan-2-ol, ethyl acetate, and methylcyclohexane as influential points.

The reason why the experimental values in the above-mentioned solvents were found to be influential is a matter of presumption. Owing to the similarity of all the diagnostic measures for 2,2,2-trifluoroethanol in both models, the lower stability of this solvent in the hydrogenation could be the reason. The detection of high-leverage points is relatively logical because, for example, triethylamine exhibited the highest nucleophilic solvation ability ($B^N = 1.38$); meanwhile, ethanol exhibited the highest Hildebrand cohesion energy density ($\delta_H^2 = 0.677$ kJ cm^{-3}), and methylcyclohexane had a zero Taft polarity characteristic π^*.

The Effect of Conversion on the Parameters Significance

Another question is whether using the simplified AKT and KP models the corrected rate of hydrogenation could be described at a selected conversion in the course of hydrogenation (see Table VII). By observation of the probabilities of the individual independent variables of the AKT and KP models, it could be possible to discuss the main factors influencing the mechanism of hydrogenation. In Table II, in addition to the corrected initial hydrogenation rates, the rates at different conversion levels are given. In some solvents, it was impossible to determine the hydrogenation rate at higher conversions due to the above-mentioned problems. Such solvents were not included in the selection

Table VI Indication of the Influential Points Using Different Diagnostic Tests

	Model AKT			Model KP		
Diagnostic Test	Influential Point	High-Leverage Point	Outlier	Influential Point	High-Leverage Point	Outlier
McCulloh–Meeter plot	1, 12	1, 12	Undetected	1, 11, 20	1, 11, 20	Undetected
Williams plot	1, 6, 8, 12, 13	1, 13	1, 6, 8, 12	1, 6, 11, 20	1, 20	1, 6, 11
Pregibon plot	1	–	–	1(S), 11, 20(S)	–	–
Jackknife residuals	Undetected	–	Undetected	1	–	1
Cook's distance	Undetected	–	–	1, 20	–	–
Atkinson's measure	1, 2, 8, 12	–	–	1, 11, 20	–	–
Belsey's DFFITS	1, 2, 8, 12	–	–	1, 11, 20	–	–
Anders–Pregibon diagnostics	1	–	–	1, 11, 20	–	–
Diagonal elements of Tukey's hat matrix	1, 13	1, 13	–	1, 11, 20	1, 11, 20	–
Diagonal elements of extended hat matrix	1	1	–	1, 11, 20	1, 11, 20	–

(S) means a strongly influential point.

Table VII Statistical Significance of the Parameters in the AKT and KP Models with Respect to Hydrogenation Conversion

Reaction Rate at Conversion	0%	20%	50%	70%
Model AKT				
Degrees of freedom	15	14	9	7
p-level				
Intercept	0.000	0.000	**0.286**	**0.836**
d	0.006	**0.059**	**0.859**	**0.312**
s	0.045	0.032	**0.161**	**0.143**
b	0.000	0.000	**0.999**	**0.271**
h	0.000	0.000	0.004	0.006
Correlation coefficient R	0.968	0.968	0.946	0.937
Model KP				
Degrees of freedom	16	15	10	8
p-level				
Intercept	0.000	0.000	0.015	0.009
A_3	0.044	0.027	**0.245**	**0.938**
A_4	0.004	0.001	0.010	0.011
A_5	0.000	0.000	**0.060**	0.037
Correlation coefficient R	0.910	0.926	0.953	0.944

for the description of the corrected rates at higher conversions. Attention was devoted to the basic statistical characteristics and the p-levels of the regression parameters.

Because of a similar interpretational meaning of the h and A_5 parameters, it can be claimed that in the whole course of hydrogenation the Hildebrand cohesion energy density of the solvent had a fundamental influence on the reaction rate. The p-level of the terms with this quantity slightly exceeded its critical limit only for the KP model at 50% conversion. On the contrary, the p-level of the terms with the π^*, β, and E_T^N variables decreased with conversion. Under its critical limit of 0.05, the parameter A_4 associated with the variable B^N was found to be significant at all conversions. The KP model gave better correlation coefficients at higher conversions (50% and 70%), whereas the AKT model gave higher correlations coefficients at lower conversions (0% and 20%). This statement must be considered with respect to the differences in degrees of freedom caused by the product precipitation in a few solvents (Table II). With respect to the lower variability in close fitting and statistical significance of the parameters, the KP model seems to be more universal.

CONCLUSIONS

For a deeper understanding of the phenomena that occur in the liquid-phase catalytic hydrogenations, the solvent effect on a model hydrogenation in the presence of a supported palladium catalyst was studied. The model reaction was the selective hydrogenation of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione to 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-diol. The kinetics of hydrogenation was studied in 21 component solvents comprising alcohols, aromatics, alkanes, ether, ester, amine, and an alkylchloride. The hydrogenation rates in the individual solvents significantly differed, and the differences were not possible to explain due to different hydrogen solubilities in the reaction mixture.

It was pointed out that the hydrogenation rate cannot be correlated with the individual physicochemical solvent properties. Therefore, the approach to the description of the reaction rates was done using the two chosen models that were originally proposed for the homogeneous liquid-phase reactions. Those models were derived on basis of the LFER principle. Both models satisfactorily described the experimental data though each one had a certain disadvantage. The AKT model gave closer fitting, but using the least-squares method it showed slight multicollinearity.

The KP model had a rather lower correlation coefficient but turned out to be universal in the evaluation of the solvent effect at any conversion. Using selected statistical diagnostic tests, it was possible to identify the most important factors of the solvent that influence the hydrogenation kinetics. In the AKT model the most important parameter was the hydrogen bond acceptor ability of the solvent, and in the KP model it was its nucleophilic solvation ability. In addition, the Hildebrand cohesion energy density contained in both models had a significant influence.

The results of this work should lead to the clarification of the solvent characteristics influencing the rate of 6-ethyl-1,2,3,4-tetrahydroanthracene-9,10-dione hydrogenation and hence help with the selection of a proper solvent system for the industrial production of hydrogen peroxide by the anthraquinone method.

ABBREVIATIONS AND SYMBOLS

A_0	Intercept in the Koppel–Palm model
A_1–A_5	Parameters in the Koppel–Palm model
a, b, d, h, s	Parameters in the Abraham–Kamlet–Taft model
AIC	Akaike information criterion
AKT	Abraham–Kamlet–Taft model
B	Nucleophilic solvation ability of the solvent
E_T	Electrophilic solvation ability of the solvent
$E_T(30)$	Dimroth–Reichardt parameter
F	Fisher F-statistics
$f(\varepsilon)$	Kirkwood function of dielectric constants
$f(n_D)$	Kirkwood function of refractive indexes
GCPR	Generalized principal component regression method
H_v^{298}	Vapor enthalpy of the solvent at 298 K, kJ mol^{-1}
KP	Koppel–Palm model
LFER	Linear free energy relationships
MEP	Mean square error of prediction
n_D	Refractive index
R	Molar gas constant, 8.314 kJ mol^{-1} K^{-1}
R	Correlation coefficient
R_{adj}	Adjusted correlation coefficient
Re_M	Reynolds number for mixing
r_0	Initial reaction rate, mmol min^{-1} g$_{\mathrm{cat}}^{-1}$
T	Reaction temperature, K
V_m^{298}	Molar volume at 298 K, cm^3 mol^{-1}
$x_{\mathrm{H_2}}$	Molar fraction of the equilibrium hydrogen solubility
XYZ	Dependent variable in the regression models
XYZ_0	Intercept in the Abraham–Kamlet–Taft model

Greek Symbols

α	Taft hydrogen bond donor ability of the solvent
β	Taft hydrogen bond acceptor ability of the solvent
δ	Correction on polarizability
δ_{H}^2	Hildebrand cohesive energy density of the solvent, kJ cm^{-3}
ε	Relative static dielectric constant
Φs	Weisz–Prater criterion
π^*	Taft polarity parameter of the solvent

Indexes

c	Corrected quantity
i	Component i
HMPA	Hexamethylphosphoric amide
N	Normalized quantity
TMS	Trimethylsilane
ξ	Conversion range

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