

A CONTRIBUTION TO THE INTERPRETATION OF SOLVENT EFFECTS ON REACTION KINETICS

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An interpretation of solvent effect on reaction rate by multi-parameter equations has been proposed under the assumption that the LFER type relations are valid in every solvent. Under the same assumption, the equations can also be applied to a system with a heterogeneous catalyst. In the latter system, the effect of solvents on the relative adsorption constants of reactants has been interpreted similarly. The newly defined parameters of solvents cannot be directly used in other reaction systems. The limited validity of the earlier one-parameter correlations is ascribed to the interference of the reactant structure. The numerical values of S_0 parameters were determined in hydrogenations (5% Pt on silica gel as catalyst) of the C=C double bond and the NO₂ group on an aromatic ring.

Numerous equations have been so far proposed to interpret the effect of solvents on the reactivity of organic compounds¹⁻¹⁵. The solvent has been mostly characterised by a physico-chemical constant or combination of these constants or by an empirical parameter defined on the basis of kinetic measurements. The application of the correlations meets with a partial success since they are limited to closely related systems only. Particularly in heterogeneous systems, such as in catalytic reactions, it is hardly possible to express the solvent effect by an one-parameter correlation.

According to the LFER method, the change of free enthalpy due to a changed structure of the reactant or a changed solvent can be expressed by the correlation

$$\Delta G = \Delta G_0 + \alpha \Delta x, \quad (1)$$

where ΔG_0 is the free enthalpy change in the reaction of a standard substance, Δx is the reaction medium change or the change in the structure of the reactant, and ΔG is the free enthalpy change accompanying the structural change of the reactant or the change of the solvent. A similar correlation governs the free energy change.

In the field of heterogeneous catalytic reactions, the LFER method has been for the first time successfully applied by Kraus¹⁶ and then used many times in correlations of reactivities and adsorptivities with the structure of reactants. The effect of all interaction types manifests itself in values of ρ , ρ^* , and σ parameters in the Hammett¹⁷, Taft¹⁸, and Taft-Pavelich¹⁹ equations. Their application to the interpretation of solvent effects on the course of chemical reactions is the object of the present work.

THEORETICAL

The rate of chemical reactions performed under identical conditions is affected by the structure of the reactant and by properties of the solvent. Taking for granted the validity of the Hammett equation (analogously, the Taft and Taft-Pavelich equation) expressing the structural effect of reactants on their reactivity in every solvent

$$\log(k/k_0)_n = \rho_n \sigma \quad (2)$$

it can be written

$$\log [(k)_n/(k)_s] = R_\rho \sigma + S_\rho, \quad (3)$$

where

$$R_\rho = (\rho_n - \rho_s) \quad \text{and} \quad S_\rho = \log [(k_0)_n/(k_0)_s].$$

Equation (3) shows dependence of the relative rate (equilibrium) constant on properties of the solvent, expressed by R_ρ and S_ρ parameters. The R_ρ (R_{ρ^*}) parameter is directly proportional to the difference of the relative free energy (free enthalpy) of the solvent n and that of the solvent s in the case of the actual and the standard reactant. The parameter S_ρ characterises the effect of the solvent change on the relative rate constant of the test-substance bearing a standard substituent. In the Hammett equation, this substituent is represented by hydrogen, the σ parameter value of which is by definition equal to zero; in the Taft (Taft-Pavelich) equation, the methyl group is used as the standard substituent ($\sigma^* = E_s = 0$). The necessary and sufficient condition for the validity of the equation (3) is the validity of the Hammett (Taft, Taft-Pavelich) equation with the same values of σ (σ^* , E_s) constants of the appropriate substituents in every solvent. The equation is independent of the reaction mechanism in the particular solvent but this mechanism must be the same for the whole model series. The application of the R_ρ parameter (and analogous parameters of this type) to systems of other reaction types (A, B) depends on the condition

$$(\rho_{n_A} - \rho_{s_A})/(\rho_{n_B} - \rho_{s_B}) = 1 \quad (4)$$

as it may be inferred from equation (3).

The difference in susceptibilities of the two systems (reaction types) must vary with the structural change within the particular reaction series in every other solvent as in the standard solvent. Since the ρ parameter expresses the susceptibility of the system to the change in the structure of reactants, the correlation (4) can be expected to be valid only in reactions of a closely related mechanism in similar structural systems.

From the Hammett equation, we may analogously infer for the heterogeneous system the equation (5) expressing dependence of the adsorption constant on the solvent

$$\log [(K/K_0)_n/(K/K_0)_s] = R_{\varrho,K}\sigma, \quad (5)$$

where $R_{\varrho,K} = \varrho_{K,n} - \varrho_{K,s}$. As it is more difficult to measure the absolute adsorption constants than the relative ones, equation (4) has not been put into two-parameter form corresponding to equation (3). The $S_{\varrho,K}$ parameter, analogous to the earlier introduced S_{ϱ} parameter is contained implicitly in the corresponding equations of Table I.

For the selectivity of competitive catalytic reactions of compounds A and B, it can be written under the same concentrations of these compounds and the same orders

$$\log [(S_{A,B})_n/(S_{A,B})_s] = (R_{\varrho} + R_{\varrho,K})\sigma, \quad (6)$$

where A designates the substituted reactant and B is the reactant with a standard substituent. If a nonstandard substituent (compound C) is being considered instead of the standard substituent (compound B), we obtain for the dependence of the selectivity on the solvent equation (7)

$$\log [(S_{A,C})_n/(S_{A,C})_s] = (R_{\varrho} + R_{\varrho,K})(\sigma - \sigma_C), \quad (7)$$

where σ_C is the polar parameter of the substituent of compound C.

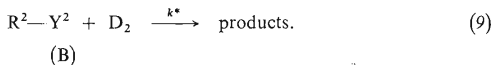
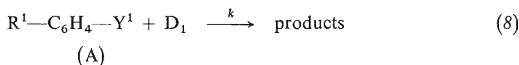
TABLE I
Correlations

Kinetic (equilibrium) parameter	Correlation of equation		
	Hammett	Taft	Taft-Pavelich
$\log \frac{k_n}{k_s}$	$R_{\varrho}\sigma + S_{\varrho}$	$R_{\varrho^*}\sigma^* + S_{\varrho^*}$	$R_{\varrho^*}\sigma^* + D_{\delta}E_s + S_{\varrho^*}$
$\log \frac{(K/K_0)_n}{(K/K_0)_s}$	$R_{\varrho,K}\sigma$	$R_{\varrho^*,K}\sigma^*$	$R_{\varrho^*,K}\sigma^* + D_{\varrho,K}E_s$
$\log \frac{(S_{A,B})_n}{(S_{A,B})_s}$	$(R_{\varrho} + R_{\varrho,K})\sigma$	$(R_{\varrho^*} + R_{\varrho^*,K})\sigma^*$	$(R_{\varrho^*} + R_{\varrho^*,K})\sigma^* + (D_{\delta} + D_{\delta,K})E_s$

$$R_{\varrho^*} = \varrho_n^* - \varrho_s^*, D_{\delta} = \delta_n - \delta_s, R_{\varrho,K} = \varrho_{K,n} - \varrho_{K,s}, R_{\varrho^*,K} = \varrho_{K,n}^* - \varrho_{K,s}^*, D_{\delta,K} = \delta_{K,n} - \delta_{K,s}$$

Similar correlations can be obtained starting from the Taft or Taft–Pavelich equation (Table I). In these correlations, the solvent is characterised by two or three parameters.

Of a special interest are the LFER type correlations for the same type of reactions in an aromatic (8) or aliphatic (9) structural system, occurring separately under analogous conditions in the solvent n



Provided that $\text{D}_1 = \text{D}_2 = \text{const.}$, the dependence of the rate or equilibrium constant k in (8) on the change of the substituent R^1 is expressed by the Hammett equation and, analogously, by the Taft equation in the case of the Scheme (9). Their combination gives

$$\log(k_n/k_n^*) = \rho_n \sigma - \rho_n^* \sigma^* + \log[(k_0)_n/(k_0^*)_n]. \quad (10)$$

Equation (10) represents dependence of the rate or equilibrium constant of the $\text{R}^1\text{—C}_6\text{H}_4\text{—Y}^1$ type reactant referred to the rate or equilibrium constant of the type $\text{R}^2\text{—Y}^2$ reactants upon the structural change of both the reactant types under consideration.

Let us consider situation when $\text{R}^1 = \text{R}^2$, $\text{D}^1 = \text{D}^2$, and $\text{Y}^1 = \text{Y}^2$ in (8) and (9). Provided that the (k/k^*) ratio would depend only on the modification of the molecule containing the reaction centre $\text{Y}^1 = \text{Y}^2$, the change of the reaction medium should not interfere. As demonstrated by Koppel and Palm¹⁰, the slopes of the plot of ρ_{rel} values obtained in esterifications of substituted benzoic acids and substituted benzylic-acetic acids as a ratio of ρ values in the particular solvent to those in methanol as standard solvent, *versus* ρ_{rel} values obtained in the case of α -substituted acetic acids, are not the same. There is no special reason why an aromatic or arylaliphatic system attached to the same reaction centre should exert a different effect on the ρ (ρ^*) parameter when compared with the aliphatic system, consequently, the interaction between the substituent and the solvent appears as established¹⁰.

In the present case, the ratio of rate constants does not exclusively depend on the structural change of the organic compound. The similarity of equations (3) and (10) indicates that the change of the solvent affects the rate or equilibrium constants in a similar manner as does the structural change. It may be inferred from equation (10) that

$$\log (k_n/k_s^*) = \rho_n \sigma - \rho_s^* \sigma^* + \log [(k_0)_n/(k_0)_s^*]. \quad (11)$$

Equation (11) combines influences of the structural change of the reactant and of the solvent change, resulting in different effects on the reaction centre of the molecule. Equation (11) as a general expression of equations (3) and (10), demonstrates the close relationship between the solvent effect and the structural effect of an organic compound and their influence on the reactivity or adsorptivity of organic compounds.

The validity of the above proposed correlations under the conditions stated is evident. We have now measured values of the S_0 parameters appearing in the above equations in hydrogenations of the double bond in aliphatic systems and in hydrogenations of aromatic nitro compounds to aromatic amines. 2,3-Dimethyl-2-butene and nitrobenzene were used as model reactants (*cf.* the earlier investigations in the field of heterogeneous hydrogenations²⁰⁻²⁴). For the application of the above proposed correlations requiring an excellent validity of the starting Hammett and Taft type equations in numerous solvents, a suitable experimental material is lacking in the field of heterogeneous hydrogenations²⁴.

EXPERIMENTAL

Materials. The 5% Pt on silica gel catalyst was prepared according to an earlier paper²⁰. The particle size below 0.063 mm was used in measurements. Cyclohexane, diethyl ether, toluene, methanol, benzene, ethyl acetate, and 1,4-dioxane were used as solvents (their purification was reported earlier²⁰). All the solvents were freshly distilled and were chromatographically homogeneous. Electrolytical hydrogen (Technoplyn, Parudubice, Czechoslovakia) was used directly. The test-substances were freshly distilled nitrobenzene (VCHZ, Parudubice, Czechoslovakia), b.p. 96°C at 1.6 kPa (12 Torr), and 2,3-dimethyl-2-butene obtained²⁵ by reaction of 2-magnesium-bromopropane with acetone and the subsequent dehydration of the resulting 2,3-dimethyl-2-butanol by means of 85% phosphoric acid. Both test-substances were chromatographically homogeneous.

Apparatus and procedure. For details see earlier papers²⁰⁻²⁴. The test-substance (1 ml) in the appropriate solvent (25 ml) was hydrogenated in an agitated reactor at 20°C and the atmospheric pressure of hydrogen over 0.04–0.08 g of the catalyst. The reaction rate was determined from the times dependence of the hydrogen uptake.

RESULTS AND DISCUSSION

Kinetic measurements were performed under such conditions that did not affect the reaction rate by mass transfer²⁰. Initial rate values in hydrogenations of 2,3-dimethyl-2-butene to 2,3-dimethylbutane and of nitrobenzene to aniline were measured in 7 solvents in the zero order region with respect to the initial concentration of the reactant. Corrections to the atmospheric pressure and tension of solvents were made²⁰⁻²⁴. For the S_0 values (methanol as standard solvent) see Table II. No correlations were found between the S_0 values in the hydrogenation of an aliphatic

double bond and the hydrogenation of an aromatic nitro group. The S_0 values determined in the present work are importance from the standpoint of the application of the above proposed multi-parameter equations to the interpretation of the solvent effect in catalytic hydrogenations.

The present results make possible the evaluation of the earlier proposed^{20,22} solvent parameters (τ' and φ) in the modified Drougard-Decrooq equation and discussion on their limitations. Thus, the τ' parameter is defined in the case of the solvent n by the expression

$$\log [(k)_n/(k)_s] = \lambda' \tau' \quad (12)$$

using the data from the hydrogenation of cyclohexene and taking $\lambda' = 1$. Methanol was selected as the standard solvent s . Comparison of equations (3) and (12) gives

$$\tau' = (R_0 \sigma + S_0) / \lambda' \quad (13)$$

The parameter τ' is thus function of the reactant structure and cannot be regarded as a constant of the solvent. Successful applications of equation (12) to closely related structural systems can be ascribed to a small difference in σ values since when $\sigma_A \doteq \sigma_B$, then $\tau'_A \approx \tau'_B$.

The solvent parameters R_0 and S_0 can be hardly used in other reaction systems but they characterise the solvent in the reaction system at hand without being dependent of the structure of reactants.

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TABLE II
The S_0 Values

Solvent	S_0 (aliph. C=C)	S_0 (arom. NO ₂)
Cyclohexane	0.41	0.01
Diethyl ether	0.54	-0.11
Toluene	0.41	-0.29
Methanol	0.00	0.00
Benzene	-1.03	-0.15
Ethyl acetate	0.23	-0.77
1,4-Dioxane	-0.10	-0.65

LIST OF SYMBOLS

D_δ	solvent parameter
E_S	steric parameter of the substituent in the Taft–Pavelich equation
ΔG	the free enthalpy change due to the change of the reaction medium or to the structural change of reactant
ΔG_0	the free enthalpy change of a standard reactant
k	rate constant (dimension according to the form of the kinetic equation)
K	adsorption coefficient (dimension according to the form of the kinetic equation)
r	reaction rate (dimension according to the form of the kinetic equation)
R_e	solvent parameter
S_e	solvent parameter
$S_{A,B}$	selectivity of the competitive reaction of compounds A and B
Δx	change of the reaction medium or of the reactant structure
α	proportionality constant
δ	parameter characterising susceptibility of the reactivity (adsorptivity) to the change of the steric parameter of the substituent in the Taft and the Taft–Pavelich equation
ρ	parameter characterising susceptibility of the reactivity (adsorptivity) to the polarity change of the substituent in the Hammett equation
ρ^*	parameter characterising susceptibility of the reactivity (adsorptivity) to the polarity change of the substituent in the Taft and the Taft–Pavelich equation
σ	polar parameter of the substituent in the Hammett equation
σ^*	polar parameter of the substituent in the Taft and the Taft–Pavelich equation

Indices

K	designation of adsorptivity
n	any solvent
s	standard solvent
0	standard substituent
*	superscript of parameters from the Taft and the Taft–Pavelich equation

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