Investigation of the reactivity of 4-pyrimidinecarboxylic, 6-hydroxy-4-pyrimidinecarboxylic and 5-hydroxyorotic acids with diazodiphenylmethane in various alcohols. Part III

FATHI H. ASSALEH[*], ALEKSANDAR D. MARINKOVIĆ[#], SAŠA Ž. DRMANIĆ[#] and BRATISLAV Ž. JOVANOVIĆ[#]

Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 3503, 11120 Belgrade, Serbia (e-mail: assaleh@tmf.bg.ac.yu)

Abstract: Rate constants for the reaction of diazodiphenylmethane (DDM) with 4-pyrimidinecarboxylic, 6-hydroxy-4-pyrimidinecarboxylic and 5-hydroxyorotic acids were determined in twelve protic solvents at 30 °C using the well known UV-spectrophotometric method. The second order rate contants for the examined acids were correlated using the appropriate solvent parameters by the equation $\log k = \log k_0 + af(\varepsilon) + b\sigma^* + cn_{\gamma H}$ were $f(\varepsilon)$ is the Kirkwood function of relative permittivity $[(\varepsilon–1)/(2\varepsilon + 1)]$, σ^* is the Taft polar constant for the alkyl group R in the alcohol ROH, and $n_{\gamma H}$ is the mumber of hydrogen atoms in the γ-position in the alcohol. The results obtained for the investigated acids were compared with the corresponding results for benzoic, 2- and 3-hydroxybenzoic acids and the influence of the structure of the investigated acids on the reactivity in hydroxylic solvents is discussed. It was also possible to evaluate and distinguish the specific and non-specific solvent effects and their influence on the reaction rate.

Keywords: rate constants, 5-hydroxyorotic acid, 6-hydroxy-4-pyrimidinecarboxylic acid, 4-pyrimidinecarboxylic acid.

INTRODUCTION

In a previous study,[1] the reactivities of 3- and 4-pyridine and 3- and 4-pyridine *N*-oxide carboxylic acids and *m*- and *p*-substituted benzoic acids with diazodiphenylmethane (DDM) in various alcohols were examined and the kinetic data were correlated with appropriate solvent parameters. It was concluded that the solvent effect is best described through multiple regression of $\log k_2$ *vs.* $f(\varepsilon)$ (the Kirkwood function of relative permitivity $[(\varepsilon - 1)/(2\varepsilon + 1)]$), σ^* (the Taft polar constant of the alcohol) and $n_{\gamma H}$ (the number of γ-hydrogen atoms in the alcohol).

Considering the mechanism of the reaction, although a larger effect of the rela-

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* Corresponding author.

\# Serbian Chemical Society active member.

tive permittivity of the alcohol was expected in this investigation, it appeared that the term σ^* was dominant.

In recent papers,[2,3] the protic and aprotic solvent effects on the reactivity of isomeric pyridine and pyridine *N*-oxide mono-carboxylic acids with DDM were examined by means of the linear solvation energy relationship (LFER) concept.[4] The correlation equations obtained according to this model by stepwise regression for all the examined acids showed that the best approach which aids in the understanding of the role of protic hydroxylic solvents in the reaction lies in the separate correlations of log k_2 with the hydrogen bond donating (HBD) and the hydrogen bond accepting (HBA) ability of the solvents.

In the present work, the second-order rate constants for the reaction of 4-pyrimidinecarboxylic, 6-hydroxy-4-pyrimidinecarboxylic and 5-hydroxyorotic acids with DDM in twelve protic solvents at 30 °C were determined. In order to explain the kinetic results in relation to solvent effects, the second-order rate constants were correlated using Eq. (1):

$$\log k = \log k_0 + af(\varepsilon) + b\sigma^* + cn_{\gamma H} \tag{1}$$

Analysis of Eq. (1), as in earlier studies, involves the σ^* value of the R group in the alcohol ROH; the Kirkwood function of the relative permittivity $f(\varepsilon) = (\varepsilon-1)/(2\varepsilon + 1)$ and $n_{\gamma H}$ the number of hydrogen atoms in the γ-position in the alcohol. This correlation affords information on the relative importance of the $f(\varepsilon)$ term (non-specific electrostatic solvent effect) and σ^* (specific solvent effect, Lewis acidity/basicity).

EXPERIMENTAL

Materials

4-Pyrimidinecarboxylic and 6-hydroxy-4-pyrimidinecarboxylic acids were prepared by known method.[5,6] 5-Hydroxyorotic acid was synthesized by application of the Elbs oxidation of orotic acid.[7] All the synthesized acids had melting points identical or very close to those reported in the literature. All the synthesized acids had satisfactory elemental analysis and the structures were confirmed by FTIR, ^{1}H- and ^{13}C-NMR spectroscopy.

6-Hydroxy-4-pyrimidinecarboxylic acid: ^{1}H NMR data (δ/ppm) (in DMSO-d_6): 6.83, C(5)-H; 8.25, C(2)-H; 12.85, COOH; in acetone-d_6: 6.99, C(5)-H; 8.33, C(2)-H; 10.55, C(6)-OH; 13.25, COOH. ^{13}C NMR data at 62.5 MHz (δ/ppm) (DMSO-d_6): 150.60, C(2); 153.12, C(4); 117.04, C(5); 161.59, C(6); 165.08, COOH.

Diazodiphenylmethane was prepared by the Smith and Howard method.[8] The stock solution of *ca*. 0.06 mol dm^{-3} was stored in a refrigerator and diluted before use.

Solvents were purified as described in the literature.[9] All the solvents used for kinetic studies were examined by GLC and no impurities were detected.

Kinetic measurements

The rate constants k for the reaction of all the investigated acids with DDM were determined spectroscopically[10] using a Shimadzu UV1700 spectrophotometer. Optical density measurements were performed at 525 nm with 1 cm cells at 30 ± 0.05 °C.

Three rate determinations were made for each acid and in every case the individual second-order rate constants agreed within 3 % of the mean.

RESULTS AND DISCUSSION

The mechanism of the reaction between a carboxylic acid and DDM involves a rate-determining proton transfer from the acid to DDM, forming a diphenyl-methanediazonium carboxylate ion-pair in the transition state.[11–14]

$$Ph_2CN_2 + RCOOH \xrightarrow{\text{slow}} Ph_2CHN_2^+ \ ^-OOCR$$
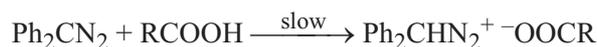
The values of the second-order rate constants for the reaction of 4-pyrimidine-carboxylic acid, 6-hydroxy-4-pyrimidinecarboxylic acid and 5-hydroxyorotic acid with DDM, determined in this work at 30 °C in twelve alcohols are given in Table I.

TABLE I. Rate constants ($dm^3 \ mol^{-1} \ min^{-1}$) for the reaction of all the investigated acids with DDM in alcohols at 30 °C

	Solvent	4-Pyrimidinecarboxylic acid	6-Hydroxy-4-pyrimi-dinecarboxylic acid	5-Hydroxyorotic acid
1.	Methanol	56.17	53.42	816.15
2.	Ethanol	28.26	25.66	485.34
3.	Propan-1-ol	30.25	20.38	437.94
4.	Propan-2-ol	19.22	13.99	338.53
5.	Butan-1-ol	25.55	19.54	426.12
6.	Butan-2-ol	18.06	12.26	318.83
7.	2-Methylpropan-1-ol	32.52	24.21	586.83
8.	2-Methylpropan-2-ol	10.12	5.05	179.19
9.	Pentan-1-ol	19.74	14.76	379.54
10.	2-Methylbutan-2-ol	5.625	2.54	121.57
11.	Cyclopentanol	23.68	11.66	288.73
12.	Benzyl alcohol	236.43	104.63	2957.9

The results of multiple linear regressions of log k for all the investigated acids with the solvent parameters ($f(\varepsilon)$, σ^*, and $n_{\gamma H}$) using Eq. (1) in the twelve alcohols are given in Table II. The corresponding correlations for benzoic and 2-hydro-xybenzoic acids calculated from literature values of log k_2,[15] as well as for 3-hydroxybenzoic acid[1] are also given in Table II. The solvent parameters $f(\varepsilon)$ and σ^* are taken from the literature.[16,17]

TABLE II. Results of the correlations of log k_2 for the investigated acids in twelve protic solvents using Eq. (1)

Acid	log $k = \log k_0 = af(\varepsilon) + b\sigma^* + cn_{\gamma H}$					
	log k_0	a^a	b^a	c^a	r^b	$s.d.^c(F^d)$
4-Pyrimidinecarboxylic acid (I)	0.826	2.045	2.700	0.007	0.990	0.065
	(±0.411)	(±0.888)	(±0.159)	(±0.011)		(131.2)
6-Hydroxy-4-pyrimidinecarboxylic acid (II)	−1.154	5.931	2.539	0.019	0.995	0.048
	(±0.303)	(±0.655)	(±0.117)	(±0.008)		(277.6)

TABLE II. Continued

Acid	$\log k = \log k_0 = af(\varepsilon) + b\sigma^* + cn_{\gamma H}$					
	$\log k_0$	$a^{[a]}$	$b^{[a]}$	$c^{[a]}$	$r^{[b]}$	$s.d.^{[c]}(F^{[d]})$
5-Hydroxyorotic acid (III)	2.252	1.455	2.408	0.018	0.987	0.064
	(±0.400)	(±0.865)	(±0.155)	(±0.010)		(104.6)
Benzoic acid (IV)	−1.489	3.971	3.020	0.032	0.994	0.057
	(±0.361)	(±0.780)	(±0.139)	(±0.009)		(225.8)
3-Hydroxybenzoic acid (V)	−1.455	3.922	3.131	0.030	0.991	0.072
	(±0.452)	(±0.976)	(±0.174)	(±0.012)		(153.6)
2-Hydroxybenzoic acid (VI)	1.293	−0.144	2.509	0.009	0.970	0.10
	(±0.630)	(±1.361)	(±0.243)	(±0.016)		(42.4)

[a]calculated coefficients; [b]r – correlation coefficient; [c] $s.d.$ – standard deviation of the estimate; [d]$F – F$ test for significance of regression

The values of the coefficients of the solvent parameters calculated from Eq. (1), are given in Table II. A favorable influence of the relative permittivity was expected for a reaction in which the passage from the initial to the transition state involves charge separation, but stepwise regression showed that the σ^* term is more important. This was taken to indicate the dominant role of the solvating properties of the alcohol, *i.e.*, the Lewis acidity/basicity of the solvent. The term $n_{\gamma H}$, which is of minor overall importance, was interpreted in terms of a steric effect which moderates the basic properties of the alcohol oxygen. For certain alcohols, it has a strong effect, *e.g.* the reaction is considerably faster in 2-methylbutan-1-ol than in ethanol, even though the former has a lower relative permittivity and a more negative value of σ^* while for 2-methylbutan-1-ol, $n_{\gamma H} = 6$ whereas for ethanol, $n_{\gamma H} = 0$. The regression coefficients b from one-parameter correlations $\log k_2$ *vs.* σ^* of the investigated acids are: 2.817 ± 0.166 ($r = 0.983$; $s.d. = 0.076$; $n = 12$); 2.89 ± 0.320 ($r = 0.943$; $s.d. = 0.142$; $n = 12$) and 2.45 ± 0.156 ($r = 0.979$; $s.d. = 0.073$; $n = 12$) for the acids (I), (II) and (III), respectively. One-parameter correlations for $\log k_2$ *vs.* $f(\varepsilon)$ are not statistically acceptable in all cases, which show that σ^* is a much more dominant parameter in comparison to the $f(\varepsilon)$ parameter.

The best method for examining the relative contribution of the $f(\varepsilon)$ parameter, which describes the non-specific solvent effect, actually its electrostatic properties, and the σ^* parameter, which describes a specific solvent effect, *i.e.,* the solvent acidity/basicity, on the reaction rate is the method proposed by Koppel and Palm.[18] According to this procedure, $\log k_2$ was correlated using a two-parameters equation (2):

$$\log k_2 = a f(\varepsilon) + b\sigma^* \qquad (2)$$

which is rearranged into equation (3) for a pair of alcohols 1 and 2:

$$\Delta\log k_2 = a[f(\varepsilon_1)-f(\varepsilon_2)] + b(\sigma_1^* - \sigma_2^*) \qquad (3)$$

By application of Eq. (3) for selected solvents pairs, the contributions of the

parameters $f(\varepsilon)$ and σ^* could be simply calculated and accordingly, their influence on the reaction rate estimated.

The obtained results calculated by this method for 4-pyrimidinecarboxylic acid are given in Table III.

TABLE III. Contribution of the $f(\varepsilon)$ and σ^* terms to $\Delta\log k_2$ selected pairs of alcohols for 4-pyrimidinecarboxylic acid

| Solvent (relative permittivity)		$\Delta\log k_2$	$1.973\ f(\varepsilon)^a$	$2.679\ \sigma^{*a}$
Methanol	(32.7)	1.02	0.190 (19 %)[b]	0.830 (71%)
2-Methylbutan-2-ol	(5.82)			
Methanol		0.605	0.058 (14 %)	0.362 (86 %)
Pentan-1-ol	(13.90)			
Methanol	(16.56)	0.420	0.042 (7 %)	0.563 (93 %)
Butan-2-ol				

[a]regression coefficients a and b are from Eq. (3); [b]percent contribution of the individual solvent effects

It is evident from Table III that the larger differences in the dielectric constant of the alcohols (*e.g.* methanol and 2-methylbutan-2-ol) on the $\Delta\log k_2$ depends more on the σ^* than on $f(\varepsilon)$ parameter. This means that the specific solvent effect (Lewis acidity/basicity of alcohol) has a dominant effect on the reaction rate in comparison to the non-specific solvent effect (electrostatic solvent effect) expressed through the $f(\varepsilon)$ parameter. For other selected pairs of alcohols, when the differences in $\Delta f(\varepsilon)$ are smaller, the contribution of the σ^* parameter is larger (Table III). A similar analysis for the other investigated acids also indicates a dominant influence of the σ^* in comparison to the $f(\varepsilon)$ parameter. Thus, this method provides a more precise analysis of the influence of solvent effects on the reaction rate.

The percent contribution of the solvent parameters $f(\varepsilon)$ and σ^* to $\Delta\log k_2$ for benzoic acid, for the same pairs of alcohols, are: 29 and 71 %; 21 and 75 %, 11 and 89 %, respectively.[19] The larger influence of the specific solvent effect (σ^*) is also observed for benzoic acid, with, however, a somewhat increased contribution of the $f(\varepsilon)$ parameter (non-specific solvent effect) as compared to 4-pyrimidinecarboxylic acid. This probably could be explained by the existence of the strong electron-accepting pyrimidinyl nucleus (–R effect of the nitrogens in the 2 and 4 position of the ring) in 4-pyrimidinecarboxylic acid, which offers the possibility for the dipolar resonance structures (1) and (2) shown in Scheme 1. These structures are in the initial state stabilized by the electrostatic solvent effect $f(\varepsilon)$, thus the change in the contribution of the parameter $f(\varepsilon)$ from the initial to the transition state (carboxylate anion in forming) will be lower in comparison to that of benzoic acid. Intercorrelation of $\log k_2$ for benzoic acid (IV) and 4-pyrimidinecarboxylic acid (I) gave the following result:

$$\log k_2\ (IV) = -\ 1.636\ (\pm 0.080) + 1.134\ (\pm 0.055)\ \log k_2\ (I) \qquad (4)$$
$$R = 0.998;\ s.d. = 0.072;\ F = 427;\ n = 12$$

(1)   (2)
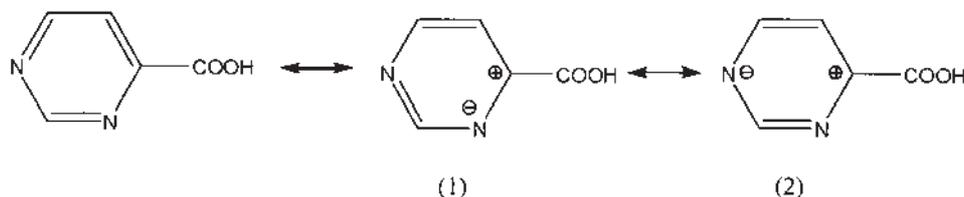
Scheme 1. Dipolar resonance structures of 4-pyrimidinecarboxylic acid.

The above intercorrelation indicates that 4-pyrimidinecarboxylic acid is less sensitive to the overall solvent effect in relation to benzoic acid (see regression coefficients a and b in Table II), which again could be attributed to the electron-acceptor character of the 4-pyrimidine nucleus in comparison to that of the phenyl, because the 4-pyrimidinecarboxylate anion is more stabilized than the benzoate anion.

According to literature data,[20] and also to a previous investigation[1] of the solvent effect on the σ value of the substituent, it appears that the m-OH substituent in the alcohols is electron-donating ($\sigma_{m\text{-OH}}$ (mean value) $= -0.112$). This is different from the value $\sigma_{m\text{-OH}}$ determined from the dissociation constant of 3-hydroxybenzoic acid in water, which is 0.12.[21]

Electron-donor properties of the m-OH substituent cause a lower acidity of 3-hydroxybenzoic acid in comparison with benzoic acid in reaction with DDM in alcohols. The same effect of lowered acidity is observed for 6-hydroxy-4-pyrimidinecarboxylic acid in comparison with 4-pyrimidinecarboxylic acid (see Table I). This was to be expected, as in both acids the OH substituent is in the *meta* position with respect to the carboxylic group.

The possibility of the existence of different tautometric forms of 6-hydroxy-4-pyrimidinecarboxylic acid, two keto (1, 2) and one enol form (3), are presented in Scheme 2, together with their corresponding resonance structures (4, 5, 6 and 7).
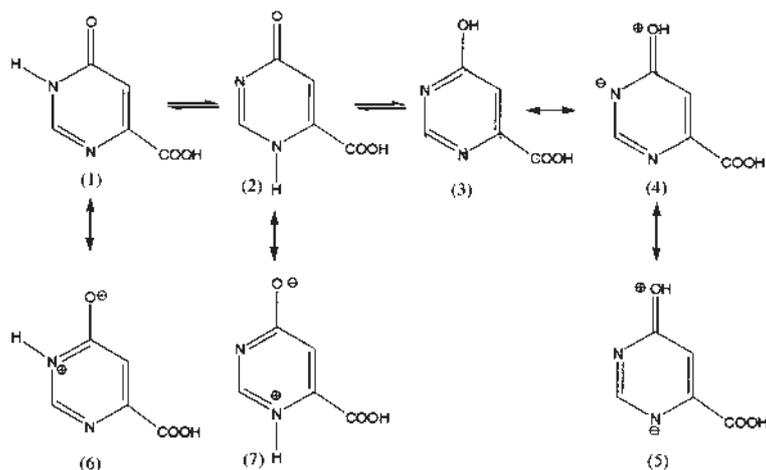
Scheme 2. Tautomeric forms of 6-hydroxy-4-pyrimidinecarboxylic acid and their corresponding resonance structures.

There are no data in the literature on the keto–enol tautomerism of this acid. The presented ^{13}C-NMR and ^{1}H-NMR data both in DMSO-d_6 and acetone-d_6 (see Experimental), could not be reliably used fot the determination of the keto–enol equilibrium in alcohols.

The diminished acidity of this acid, in comparison with 4-pyrimidinecarboxylic acid, could probably be explained by the existence of the enol form (3) in alcohol, either as the sole or the dominant form in the corresponding equilibrium (Scheme 2). The resonance structure (5) indicates the possibility of an intramolecular hydrogen bond between the carboxy group hydrogen and the ring nitrogen with increased electron density, which could also contribute to lower acidity of this acid.

Intercorrelation of the log k_2 values of 3-hydroxybenzoic acid (V) and 6-hydroxy-4-pyrimidinecarboxylic acid (II) gave the following result:

$$\log k_2 \text{ (V)} = -1.471 \ (\pm 0.088) + 1.093 \ (\pm 0.068) \log k_2 \text{ (II)} \qquad (5)$$
$$R = 0.981; \ s.d. = 0.095; \ F = 259; \ n = 12$$

The above intercorrelation indicates a lower sensitivity of 6-hydroxy-4-pyrimidinecarboxylic acid to the overall solvent effect in comparison with 3-hydroxybenzoic acid. Also, for this pair of acids the contribution of the solvent effect expressed through the σ^* parameter on $\Delta \log k_2$ predominates, having a value of 73 % for 3-hydroxybenzoic acid and 58 % for 6-hydroxy-4-pyrimidinecarboxylic acid. The increase in the contribution of the $f(\varepsilon)$ parameter for the latter acid is considerable (48 %), which could probably be explained by a higher contribution of dipolar structures (Scheme 2), which is not possible in the case of 3-hydroxybenzoic acid.

The above intercorrelation indicates the structural similarity of these two acids regarding the presence of the OH substituent in the 3-position to the carboxylic group in both acids or the existence of the enol tautomer in the alcohol, whereby the OH substituent in both acids attains electron-donor character.

The considerable increase of the reaction rate constants for 2-hydroxybenzoic acid (salicylic acid) in respect to those for benzoic acid has been exhaustively explained in the literature. The fast proton transfer from the carboxylic group to DDM in the former is caused by the creation of an intramolecular hydrogen bond between the 2-hydroxy group and the negatively charged oxygen of the carboxylate anion in forming (favorable hydrogen bonding). Regression analysis of the kinetic data for salicylic acid in twenty two alcohols[9] according to Eq. (1) gave unsatisfactory results in that the correlation coefficient was poor, the standard deviation very high and the standard errors for the regression coefficients at $f(\varepsilon)$ and $n_{\gamma H}$ were very high, amounting to (1.707 ± 1.148) and (0.0157 ± 0.0167), respectively. However the solvent influence on log k_2 of salicylic acid could be satisfactorily correlated with σ^*.[15] Our correlation of literature values for 2-hydroxybenzoic acid in twelve alcohols from Table II also show the above deficiencies.

The exceptionally high reactivity of 5-hydroxyorotic acid could be explained by the formation of an intramolecular hydrogen bond of the type given in Scheme 3.
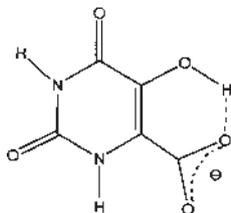
Scheme 3. Intramolecular hydrogen bonding in 5-hydroxyorotic acid.

The kinetic results for this acid could not be compared with those for orotic acid due to insolubility of the latter in alcohol. However, the results of the investigation of these two acids in dimethylformamide show a higher reactivity of 5-hydroxyorotic acid, *i.e.*, a reaction constant of 53.4 as compared to 8.7 dm^3 mol^{-1} min^{-1} for orotic acid, which corroborates the existence of hydrogen bonding in 5-hydroxyorotic acid.

Intercorrelation of log k_2 for 4-pyrimidinecarboxylic acid (I) and 5-hydroxyorotic acid (III) gives the following result:

$$\log k_2 \text{ (I)} = -1.567 \ (\pm 0.142) + 1.134 \ (\pm 0.053) \log k_2 \text{ (III)} \qquad (6)$$
$$R = 0.989; \ s.d. = 0.061; \ F = 450; \ n = 12$$

5-Hydroxyorotic acid is less sensitive to the overall solvent effect, in comparison with 4-pyrimidinecarboxylic acid, because the stabilization of the corresponding anion is achieved by the formation of the intramolecular hydrogen bond (Scheme 3). However, the effect of the parameter σ^* on the reactivity of 5-hydroxyorotic acid is also dominant, having higher value than for 4-pyrimidinecarboxylic acid: 85 %, 89 % and 95 % for the pairs of alcohol from Table III, respectively.
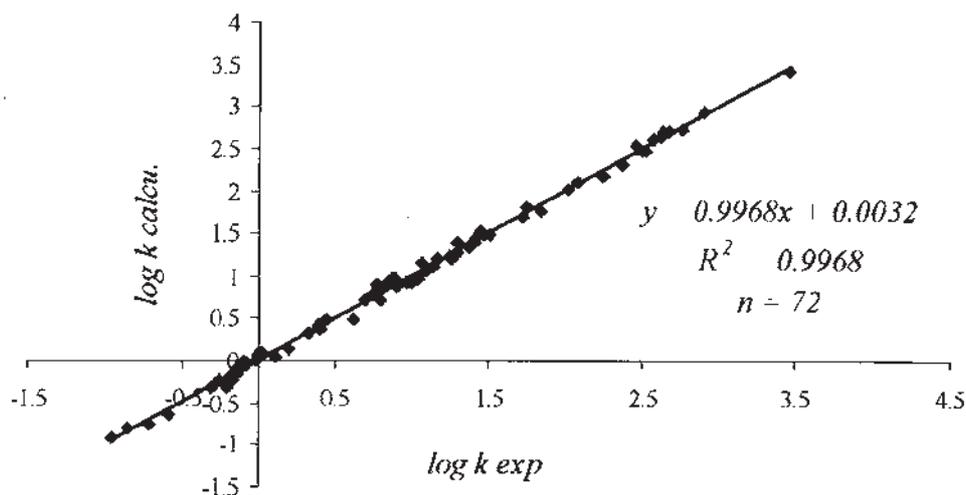

Fig. 1. Intercorrelation of log k calculated and log k observed for all the acids in all the employed alcohols.

This small increase of a specific solvent effect in respect to 4-pyrimidinecarboxylic acid could probably be attributed to the solvation of the hydrogen atoms at the ring nitrogen (Lewis basicity), or to the solvation of the oxygen atom of the carbonyl groups (Lewis acidity).

The degree of success of all correlations presented in present work is shown in Fig. 1, by means of a plot of log k calculated *vs.* log k obtained experimentally for all the investigated acids in all the employed alcohols.

CONCLUSION

On the basis of the information presented, it may be concluded that the solvatochromic equation (1) is applicable to the kinetic data for the reaction of the investigated acids with DDM in various alcohols. Satisfactory correlations of the kinetic data by Eq. (1) indicate that the correct models were selected. This means that these models give correct interpretations of the solvent effects with different properties of the investigated systems. According to the above results, the presented model may be used for a quantitative estimation and separation of the overall solvent effects into initial and transition state contributions in the reaction of investigated acids with DDM.

The results of the present investigations show that diverse solvent effects could be generally quantified by the use of the solvatochromic equation, although the quantitative separation of these solvent effects into individual contributions to the transition and initial states, applying mathematical treatment, was not completely possible due to the diversity of the polar structures of the investigated acids.

ИЗВОД

ИСПИТИВАЊЕ РЕАКТИВНОСТИ 4-ПИРИМИДИНКАРБОКСИЛНЕ, 6-ХИДРОКСИ-4-ПИРИМИДИНКАРБОКСИЛНЕ И 5-ХИДРОКСИОРОТИНСКЕ КИСЕЛИНЕ СА ДИАЗОДИФЕНИЛМЕТАНОМ У РАЗЛИЧИТИМ АЛКОХОЛИМА

FATHI H. ASSALEH, АЛЕКСАНДАР Д. МАРИНКОВИЋ, САША Ж. ДРМАНИЋ и БРАТИСЛАВ Ж. JOBAHOBИЋ

Технолошко-металурики факултет, Универзитет у Београду, Карнегијева 4, п. пр. 3503, 11120 Београд

Константе брзина реакција диазодифенилметана (DDM) са 4-пиримидинкарбоксилном, 6-хидрокси-4-пиримидинкарбоксилном и 5-хидроксиоротинском киселином су одређене у дванаест протичних растварача на 30 °C коришћењем познате UV-спектрофотометријске методе. Константе брзина реакција другог реда су корелисане са одговарајућим параметрима растварача коришћењем солватохромне једначине у следећем облику: log k = log k_0 + $af(\varepsilon)$ + $b\sigma^*$ + $cn_{\gamma H}$ где је број $f(\varepsilon)$ Kirkwood-ова функција $[(\varepsilon - 1)/(2\varepsilon + 1)]$ релативне пермитивности, σ^* је Taft-ова константа алкил-групе R алкохола ROH, и $n_{\gamma H}$ је број γ-водоникових атома. Добијени резултати су поређени са резултатима корелација за бензоеву, као и 2- и 3-хидроксибензоеву киселину како би се дискутовао утицај структуре испитиваних киселина у хидроксилним растварачима на њихову реактивност. Такође су процењени специфични и неспецифични ефекти растварача и њихов утицај на брзину испитиваних реакција.

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