The kinetics of the reactions of 2-substituted nicotinic acids with diazodiphenylmethane in various alcohols

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Abstract: The rate constants of 2-substituted nicotinic acids in reaction with diazodiphenylmethane (DDM) in eight alcohols at 30 ºC have been determined. In order to explain the obtained results through solvent effects, the second order reaction rate constants (k) of the examined acids were correlated using the appropriate solvent parameters by the equation:

$$\log k = \log k_0 + af(\varepsilon) + b\sigma^* + c\, n_{\gamma H}$$

where $f(\varepsilon)$ is the measure of solvent ability as a dielectric to stabilize the separation of opposite charges in the activated complex, σ^* is the measure of solvent ability to stabilize proton in the initial state and $n_{\gamma H}$ represents the ability of protic solvents to form hydrogen bond with the negative end of the ion-pair intermediate. These constants were correlated also by using solvatochromic equation of the form:

$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta$$

where π^* is the measure of the solvent polarity, α represents the scale of the solvent hydrogen bond donor acidities (HBD) and β represents the scale of the solvent hydrogen bond acceptor basicities (HBA). The correlations of the kinetic data were carried out by means of multiple linear regression analysis. The results obtained for 2-substituted nicotinic acids were compared with the results for *ortho*-substituted benzoic acid under the same experimental conditions.

Keywords: 2-substituted nicotinic acids, kinetic measurements, protic solvents, solvent parameters, diazodiphenylmethane.

INTRODUCTION

In the connection with our study of the transmission of polar effects through the pyridine ring, in this paper we extend our previous work[1–3] to a study of the reactivity of

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2-substituted nicotinic acids in their reaction with DDM in eight different alcohols. All the determined rate constants have been measured at 30 ºC. Our intention was to investigate the influence of the hydroxylic solvents in a system with a possibility of the secondary steric effects of *ortho*-substituents such as it is in 2-substituted nicotinic acids.

According to the structural analogy between the *ortho*-substituted benzoic acids (System 1) and 2-substituted nicotinic acids (System 2) it seemed of interest to compare the results of the reaction of these acids with DDM under the same experimental conditions and with identical substituents.

$$X = H; CH_3; Cl; OH; SCH_3$$

RESULTS AND DISCUSSION

The second order rate constants for the reaction of 2-substituted nicotinic acids with DDM in various alcohols at 30 ºC are given in Table I. For comparison, rate constants for equally substituted benzoic acids[4] are also given there. The results show that the rate constants increase with increasing polarity of the solvents. This is in accordance with the proposed mechanism of the reaction[5–8] between carboxylic acids and DDM which involves the rate-determining proton transfer from the acid to DDM to form a diphenylmethanediazonium carboxylate ion-pair in the transition state.[5–8]
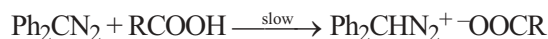
$$Ph_2CN_2 + RCOOH \xrightarrow{\text{slow}} Ph_2CHN_2^{+\ -}OOCR$$

TABLE I. Rate constants ($dm^3mol^{-1}min^{-1}$) for the reaction of 2-substituted nicotinic acids and *ortho*-substituted benzoic acids with DDM at 30 ºC in various alcohols.

Solvent	*ortho*-Substituted benzoic acids[a]					2-Substituted nicotinic acids				
	H	Cl	OH	CH$_3$	SCH$_3$	H[b]	Cl	OH	CH$_3$	SCH$_3$
Methanol	2.47	13.0	17.6	2.39	4.86	10.7	38.1	44.8	9.77	10.1
Ethanol	0.99	4.89	7.49	0.90	2.04	5.40	22.2	28.3	4.80	4.30
Butan-2-ol	0.64	3.54	6.33	0.54	1.36	3.45	9.40	12.1	2.70	2.70
Cyclopentanol	0.74	2.74	6.50	0.57	1.06	3.67	9.27	10.7	2.70	3.10
2-Me-butan-2-ol	0.14	0.87	2.80	0.10	0.26	1.26	3.42	4.72	0.76	0.81
Pentan-1-ol	0.83	3.87	5.92	0.67	1.60	3.72	11.1	15.9	3.00	3.57
2-Me-propan-1-ol	1.62	8.16	11.1	1.44	3.27	6.97	20.1	27.0	5.20	6.30
Benzyl alcohol	9.15	41.6	69.6	7.16	15.5	26.5	100.9	137.1	23.1	24.2

[a]Ref. 4, [b]Ref. 1.

The log k values of the investigated acids in all the alcohols used show a linear correlation with the corresponding literature values[4] of log k for the reaction of benzoic acid with DDM at 30 ºC in the same solvents. The correlation coefficients r are in the range ($r = 0.998$–0.977) and standard deviations s in the range ($s = 0.037$–0.023). Such linear free-energy intercorrelations indicate that the same solvent properties influence the reactivity of benzoic acids and the investigated 2-substituted nicotinic acids.

All investigated 2-substituted nicotinic acids are more reactive than correspondingly substituted benzoic acids in all the solvents used. This is understandable, considering the highly electron attracting pyridine nucleus. In both reaction series, *ortho*-hydroxy substituted acids are stronger than other substituted acids. This is generally accepted to be due to the existence of hydrogen bond interaction of the "favourable" type,[4] between the hydrogen from *ortho*-hydroxy group substituent and the carboxylic hydroxy group oxygen. This interaction is potentially possible in both salicylic acid and 2-hydroxynicotinic acid, and is probably responsible for enhanced acidity by facilitating the release of proton from the initial state to that of the activated complex.

Our previous investigations of reactivity of 6-substituted nicotinic and *para*-substituted benzoic acids with DDM in various alcohols[3] and earlier work of Chapman *et al.*[9] have established that the solvent effect is best interpreted in terms of the following properties: (a) the behavior of the solvent as a dielectric in facilitating the separation of opposite charges in the formation of the activated complex; (b) the ability of the medium to solvate the carboxylic proton and thus stabilize the initial state relative to the transition state; and (c) the ability of protic solvents to form hydrogen bonds with the negative ends of the ion-pair, and thus stabilize the transition state relative to the initial state.

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

In Eq. (1) the Kirkwood function[10] of the relative permittivity ε_r, $f(\varepsilon) = (\varepsilon_r - 1)/(2\varepsilon_r + 1)$ is a suitable measure of (a) while (b) and (c) together are governed mainly by the polar effect of the alkyl group of the alcohol appropriately expressed by the Taft polar substituent constant σ^*.[11] Steric moderation of (b) also occurs, and this is suitably accounted for by $n_{\gamma H}$, the number of γ-hydrogen atoms in the alcohol.

The solvent parameters for the alcohol solvents used are shown in Table II.

TABLE II. Solvent parameters ε_r, $f(\varepsilon) = (\varepsilon_r - 1)/(2\varepsilon_r + 1)$, σ^*, $n_{\gamma H}$

Solvent	ε	$f(\varepsilon)$	σ^*	$n_{\gamma H}$
Methanol	32.70	0.477	0.000	0
Ethanol	24.55	0.470	–0.100	0
Butan-2-ol	16.56	0.454	–0.210	3
Cyclopentanol	15.80	0.454	–0.150	0
2-Me-butan-2-ol	5.82	0.381	–0.310	3
Pentan-1-ol	13.90	0.448	–0.135	2
2-Me-propan-1-ol	17.93	0.459	–0.125	6
Benzyl alcohol	12.80	0.444	0.215	0

The results of multiple linear regressions of log k obtained from Eq. (1) for the acids from Table I with the solvent parameters $f(\varepsilon)$, σ^*, and $n_{\gamma H}$ in the eight alcohols are given in Table III.

TABLE III. Coefficients of $f(\varepsilon)$, σ^*, and $n_{\gamma H}$ for investigated carboxylic acids in eight alcohols

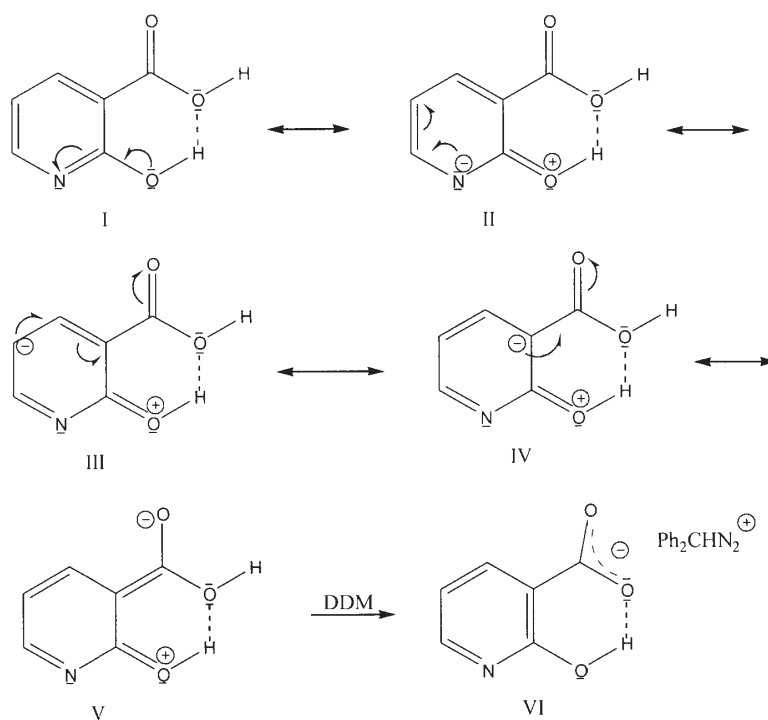| Acids	a $(f(\varepsilon))$	b (σ^*)	c $(n_{\gamma H})$	r	s
Nicotinic acid	2.678 ($\pm$ 0.677)	2.424 ($\pm$ 0.140)	0.032 ($\pm$ 0.009)	0.9959	0.047
2-Cl-Nicotinic acid	3.001 ($\pm$ 1.296)	2.686 ($\pm$ 0.268)	0.025 ($\pm$ 0.018)	0.9885	0.089
2-OH-Nicotinic acid	2.781 ($\pm$ 1.547)	2.684 ($\pm$ 0.320)	0.036 ($\pm$ 0.021)	0.9959	0.047
2-CH$_3$-Nicotinic acid	3.950 ($\pm$ 0.742)	2.560 ($\pm$ 0.154)	0.028 ($\pm$ 0.010)	0.9961	0.051
2-SCH$_3$-Nicotinic acid	3.806 ($\pm$ 0.473)	2.613 ($\pm$ 0.098)	0.039 ($\pm$ 0.006)	0.9984	0.033
Benzoic acid	3.991 ($\pm$ 0.591)	3.200 ($\pm$ 0.122)	0.048 ($\pm$ 0.008)	0.9982	0.041
2-Cl-Benzoic acid	3.485 ($\pm$0.785)	3.088 ($\pm$ 0.163)	0.051 ($\pm$ 0.011)	0.9965	0.054
2-OH-Benzoic acid	0.170($\pm$1.210)	2.850 ($\pm$ 0.251)	0.033 ($\pm$ 0.017)	0.9885	0.084
2-CH$_3$-Benzoic acid	5.518 ($\pm$ 0.473)	3.201 ($\pm$ 0.098)	0.052 ($\pm$ 0.007)	0.9990	0.033
2-SCH$_3$-Benzoic acid	4.960 ($\pm$ 0.485)	3.080 ($\pm$ 0.100)	0.054 ($\pm$ 0.007)	0.9988	0.033

After analyzing the coefficients in Table III it can be said that the influence of the relative solvent permittivity $f(\varepsilon)$ as a term of the Kirkwood function, on the reactivity of the *ortho* substituted benzoic acids is more important than in the nicotinic acids substituted at the 2-position, except for *ortho*-hydroxybenzoic acid.

The low value of the regression coefficient of the $f(\varepsilon)$ term in 2-hydroxybenzoic acids had been extensively studied before.[4] Aslan, Burden, Chapman and Shorter examined the reactivity of benzoic and salicylic acids with DDM in 22 alcohol solvents. The obtained rate constants were correlated with solvent parameters according to Eq. (1), and the calculated values of the coefficient a of the $f(\varepsilon)$ term were 3.957 for benzoic acid and 1.707 for salicylic acid. The authors suggest that this discrepancy is caused by the "external aspect" of the substituent, that is, what is presented towards the surrounding solvent molecules. Essentially electronegative groups, which mainly direct their electron clouds towards the solvent, such as –OH, orientate the solvent molecules so strongly, that it matters little which alcohol is there and what is its dielectric constant and its ability to separate charges in the transition between the initial state and the activated complex, *i.e.*, the ion pair intermediate. This investigation was further extended to the study in 10 alcohols, and it was shown that in extreme cases such as –OH, –SO$_2$Me and –NO$_2$ substituents the coefficient of $f(\varepsilon)$ is zero.

It should be noted that in the above investigation the correlation in 22 alcohols was satisfactory for benzoic acid, while for salicylic acid the regression coefficients were low (r = 0.947, s = 0.127). This was explained as a consequence of intramolecular hydrogen bonding in a competition with the intermolecular hydrogen bonding of the solvent –OH groups to the electrons of the benzene ring.

In our investigation, for the reaction with DDM in eight alcohol solvents, the coefficient of the $f(\varepsilon)$ term for 2-hydroxynicotinic acid compared to that of nicotinic acid and other substituted nicotinic acids, appears to be normal indicating that alcoholic solvents exercise their ability to facilitate the separation of opposite charges in the activated complex. However, the coefficient of $f(\varepsilon)$ for 2-hydroxynicotinic acid is much higher than that for salicylic acid (Table III), although the same type of intramolecular hydrogen bond is possible in both acids. For this, there are two possible explanations:

1. If the above reasoning of Aslan *et al.*[4] is accepted, the different behaviour of the two acids towards the dielectric properties of the solvents would be that the lone pairs on oxygen of the *ortho* –OH group in 2-hydroxynicotinic acid are less effective in disarranging the solvent molecules. The only possible conclusion is that it is less "electronegative" than the same group in salicylic acid. Taking that the pyridine nucleus itself is a highly electron-withdrawing structure, and that –OH group is also a highly electron-donating group, the folliwing resonance hybrid could be written:
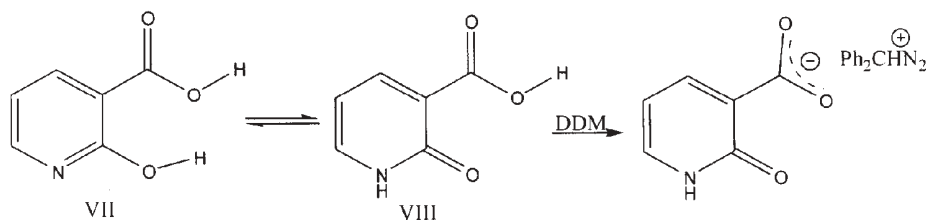

The resonance interaction I-II is highly probable, and the other electronic structures may seem elaborate, but the positive charge on oxygen must increase the strength of the hydrogen bond and consequently increase the acidity. The effect of "electronegativity" is decreased, hence the value of the coefficient of the $f(\varepsilon)$ term is similar to those for other 2-substituted nicotinic acids.

On the other hand, the increased electron density in the pyridine nucleus lowers the strength of 2-hydroxynicotinic acid by both inductive and resonance effect. While it is still

by far the strongest acid in the two series, the ratio k_2 (salicylic acid)/k_2 (benzoic acid) is twice as high as the ratio k_2 (2-hydroxynicotinic acid)/k_2 (nicotinic acid).

2. Alternatively, if in the solvents used for this investigation, the pyridine/pyridone equilibrium is very much shifted to the right, there is no hydrogen bond but this is still a

very strong acid as the pyridone system is also highly electron withdrawing. The importance of the solvent as a dielectric for stabilization of the carboxylate anion in the transition state, increases the coefficient of $f(\varepsilon)$ and it would be as observed.

However, the second alternative is much less likely, considering the resonance stabilised structure I-V, where hydrogen is positioned between the two more negative oxygen atoms, in a planar six-membered delocalized ring, constituting one of the strongest known hydrogen bonds of the chelate type.[12] Also, in the transition state, the carboxylate anion present in the ion pair (VI) is much more thermodynamically stable than the anion obtained by the proton transfer from pyridone structure (VIII).

The polarity of the solvent alkyl group, expressed by Taft polar constants σ^*, is considered to have the main influence on the rate of the chemical reactions in alcohols as solvents.[13] The influence of polarity of the solvent alkyl group is more pronounced on the reactivity of the *ortho*-substituted benzoic acids. This is as expected, as 2-substituted nicotinic acids are stronger acids, and the intervention of the solvent is not vital to facilitate the proton transfer in reaction with DDM. The $n_{\gamma H}$ term is generally needed to account for the observed rate- enhancing effect of branching at the β-carbon atom of the alcohols.[13] In this work, the $n_{\gamma H}$ term is statistically insignificant which shows that the steric effects of the solvents have a little influence on the reactivity of investigated acids.

In the present paper effects of the solvents on the rate constants were also examined by using solvatochromic equation[14] of the form:

$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta \tag{2}$$

In Eq. (2) π^* is the index of the solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by its own dielectric effects. The π^* scale was selected to run from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide. The α coefficient represents the solvent hydrogen bond donor (HBD) acidity, in other words it describes the ability of a solvent to donate a proton in the solvent-to-solute hydrogen bond. The α scale extends from 0.00 for non-HBD solvents to about 1.00 for methanol. The β coefficient is a measure of a solvent hydrogen bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton in the solute-to-solvent hydrogen bond. The β scale was selected to extend from 0.00 for non-HBA solvents to about 1.00 for hexamethylphosphoric acid triamide.

The used solvent parameters π^*, α and β are from the literature[15] and are given in Table IV.

TABLE IV. Solvent parameters π^*, α and β

Solvent	π^*	α	β
Methanol	0.60	0.98	0.66
Ethanol	0.54	0.86	0.75
Butan-2-ol	0.40	0.69	0.80
Cyclopentanol	0.45	0.66	0.84
2-Me-butan-2-ol	0.41	0.42	0.93
Pentan-1-ol	0.40	0.84	0.86
2-Me-propan-1-ol	0.40	0.79	0.84
Benzyl alcohol	0.98	0.60	0.52

The correlation analysis of investigated acids with solvent parameters π^*, α and β in protic solvents showed that there were no satisfactory results for correlation coefficients in the three-parameter Eq. (2), as it was not possible to separate individual solvent effects. Further examination using one- and two-parameter equations with π^*, α and β showed that best results are obtained by using the following forms:

$$\log k = \log k_0 + s\pi^* + a\alpha \tag{3}$$

$$\log k = \log k_0 + b\beta \tag{4}$$

These correlations are carried out for seven solvents (Table I), without 2-methylpropan-1-ol which deranged the correlation. The results from these correlations are given in the Tables V and VI:

TABLE V. Coefficients of π^* and α for investigated carboxylic acids in seven alcohols

Acids	$s(\pi^*)$	$a(\alpha)$	r	s
Nicotinic acid	1.75 ($\pm$ 0.14)	0.76 ($\pm$ 0.13)	0.9901	0.072
2-Cl-Nicotinic acid	2.01 ($\pm$ 0.06)	0.91 ($\pm$ 0.06)	0.9986	0.031
2-OH-Nicotinic acid	1.94 ($\pm$ 0.19)	0.85 ($\pm$ 0.18)	0.9855	0.097
2-CH$_3$-Nicotinic acid	1.89 ($\pm$ 0.14)	0.98 ($\pm$ 0.13)	0.9922	0.072
2-SCH$_3$-Nicotinic acid	1.856 ($\pm$ 0.19)	0.95 ($\pm$ 0.18)	0.9848	0.098
Benzoic acid	2.26($\pm$ 0.28)	1.05 ($\pm$ 0.26)	0.9777	0.143
2-Cl-Benzoic acid	2.17 ($\pm$ 0.25)	0.96 ($\pm$ 0.23)	0.9804	0.127
2-OH-Benzoic acid	2.02 ($\pm$ 0.22)	0.45 ($\pm$ 0.20)	0.9797	0.114
2-CH$_3$-Benzoic acid	2.28 ($\pm$ 0.26)	1.25 ($\pm$ 0.24)	0.9823	0.133
2-SCH$_3$-Benzoic acid	2.17 ($\pm$ 0.27)	1.14 ($\pm$ 0.25)	0.9790	0.137

TABLE VI. Coefficients of β for investigated carboxylic acids in seven alcohols.

Acids	$b(\beta)$	r	s
Nicotinic acid	–2.97 (± 0.29)	0.9778	0.096
2-Cl-Nicotinic acid	–3.40 (± 0.33)	0.9778	0.110
2-OH-Nicotinic acid	–3.23 (± 0.31)	0.9788	0.105
2-CH$_3$-Nicotinic acid	–3.31 (± 0.37)	0.9695	0.126
2-SCH$_3$-Nicotinic acid	–3.21 (± 0.44)	0.9563	0.148
Benzoic acid	–3.85 (± 0.53)	0.9566	0.178
2-Cl-Benzoic acid	–3.70 (± 0.41)	0.9713	0.137
2-OH-Benzoic acid	–3.19 (± 0.31)	0.9778	0.103
2-CH$_3$-Benzoic acid	–4.02 (± 0.56)	0.9543	0.190
2-SCH$_3$-Benzoic acid	–3.80 (± 0.52)	0.9562	0.176

Analysis of the calculated parameters in the above Tables V and VI indicates a definite regularity of the solvent effects on the investigated kinetics of both series of acids. Some general conclusions about solvent effects and their significance for the reaction rates of investigated acids are:

1. Solvent effects quantitatively expressed as coefficients s, a and b are generally higher in 2-substituted benzoic acids regarding all solvent parameters π^*, α and β, with the only exception of 2-hydroxybenzoic acid, what is explained in the text which follows. Opposedly, the reaction rates are in all experiments significantly higher for 2-substituted nicotinic acids. This is explained by the electron-attracting effect of the pyridine nitrogen atom whereby the proton is easier released and there is a better stabilization of the transition states of substituted nicotinic acids. This decreases the solvent influence on the reaction rate in the nicotinic acids series.

2. Kinetic results show that with an increase in solvent polarity, the reaction rates are also increased giving the positive sign of the coefficient π^* in corresponding correlations. Dipolar solvent effect is more pronounced in the series of substituted benzoic acids than in 2-substituted nicotinic acids because the aromatic entity in the former is more polarizable than in the latter.

3. Sign of the α coefficients is also positive in all equations, which means that there exists an electrophilic stabilization of the transition state. This stabilization is explained by the existence of a hydrogen bond interaction between the carboxylate anion and the proton of protic solvent molecule. Stabilization of carboxylate anion of both investgated series of acids is more pronounced for 2-substituted benzoic acids, which is probably caused by influences of the pyridine ring in the series of 2-substituted nicotinic acids. Effect of both inductive and resonance stabilization of the negative charge on the carboxylate anion in 2-substituted nicotinic acids decreases the necessity of electrophilic solvation, in that way decreasing solvent influences on reaction of these acids. The only exception is unexpect-

edly small value of the coefficient of α in 2-hydroxybenzoic acid, which is due to the strong hydrogen bond that exists both in the ground and is much stronger in the transition state, and is a stabilising factor itself. Therefore the solvent influence on the reaction rate is less pronounced. The difference in the coefficient of the α term in equation (2) for salicylic acid (0.45) and 2-hydroxynicotinic acid (0.85) calls for attention. Granted that a strong hydrogen bond stabilisation of the carboxylate anion in the transition state exists in both acids, the demand for electrophilic stabilisation should be about the same. However in the molecule of 2-hydroxynicotinic acids, highly nucleophilic nitrogen atom also needs electrophilic stabilization, and hence the elevated value of the coefficient of the α term.

4. The sign of the coefficients of the β term is negative in all equations, which is expected considering that this parameter defines the nucleophilic stabilization of the ground state which is slowing down the chemical reaction. Solvation of the proton in the ground state is the most significant solvent effect on reaction rates influencing their decrease. Unexpectedly smaller influence of solvent basicity on reaction rates in case of 2-substituted nicotinic acids can be understood as additive influences of solvent proton on the electron pair of the pyridine nitrogen. This effect increases the acidity of the carboxylic proton which on the other hand is stabilized by solvent which is an overall effect displayed in smaller values of the coefficient β.

EXPERIMENTAL

Materials: Commercial samples of the acids were recrystallised, and they had m.p.s identical or very close to those recorded in the literature.

Diazodiphenylmethane was prepared by Smith and Howard's method,[16] 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.[17] All the solvents used for kinetic studies were examined by GLC and no impurities were detected.

Kinetic measurements. – Rate constants k, for the reaction of 2-substituted nicotinic acids with DDM were determined as reported previously by the spectroscopic method of Roberts and his co-workers[18] using a Shimadzu 160A spectrophotometer. Optical density measurements were performed at 525 nm with 1 cm cells at 30 ± 0.05 ºC.

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

И З В О Д

КИНЕТИКА РЕАКЦИЈА 2-СУПСТИТУТИСАНИХ НИКОТИНСКИХ КИСЕЛИНА СА ДИАЗОДИФЕНИЛМЕТАНОМ У РАЗЛИЧИТИМ АЛКОХОЛИМА

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У овом раду одређене су константе брзине реакције естерификације 2-супституисаних никотинских киселина са супституентима H, Cl, OH, SCH$_3$ и CH$_3$ у осам алкохолних растварача коришћењем познате UV-спектрофотометријске методе. Добијени резултати константи бр-

зина реакције 2-супституисаних никотинских киселина као и литературних података за *орԯо*-суп-стиуисане бензоеве киселине корелисани су коришћењем једначине облика:

$$\log k = \log k_0 + af(\varepsilon) + b\sigma^* + c\,n_{\gamma\mathrm{H}}$$

где $f(\varepsilon)$ дефинише меру стабилизације раздвојених наелектрисања у прелазном стању диелектричним својствима растварача, σ^* дефинише меру стабилизације карбоксилатног протона растварачем полазног стања и $n_{\gamma\mathrm{H}}$ дефинише меру могућности грађења водоничне везе растварача са негативним крајем јонског пара. Добијени резултати су такође корелисани коришћењем солватохромне једначине облика:

$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta$$

где π^* представља меру поларности растварача, α дефинише киселост растварача као донора протона у интеракцији грађења водоничне везе (HBD), и β дефинише базност растварача као акцептора протона у интеракцији грађења водоничне везе (HBA). Дискутовани су добијени резултати за коефицијенте вишеструке регресионе анализе обе једначине који су дали задовољавајуће зависности корелација константи брзина са параметрима растварача. Добијени резултати су показали да су утицаји растварача више изражени код *орԯо*-супституисаних бензоевих киселина, него код 2-супституисаних никотинских киселина. Изузетак је *ortho*-хидрокси-бензоева киселина на коју, због изузетно израженик водоничних веза, растварачи мање утичу.

REFERENCES

1. B. Jovanović, S. Drmanić, M. Mišić-Vuković, *J. Chem. Res. (S)* (1998) 554
2. S. Drmanić, B. Jovanović, M. Mišić-Vuković, *J. Serb. Chem. Soc.* **65** (2000) 847
3. S. Drmanić, B. Jovanović, M. Mišić-Vuković, *J. Serb. Chem. Soc.* **65** (2000) 481
4. M. H. Aslam, A. G. Burden, N. B. Chapman, J. Shorter, M. Charton, *J. Chem. Soc. Perkin Trans. 2* (1981) 500
5. N. B. Chapman, J. Shorter, J. H. P. Utley, *J. Chem. Soc.* (1962) 1824
6. K. Bowden, N. B. Chapman, J. Shorter, *J. Chem. Soc.* (1963) 5329
7. A. Buckley, N. B. Chapman, J. Shorter, *J. Chem. Soc.* (1965) 6310
8. K. Bowden, *Can. J. Chem.* **43** (1965) 3354
9. N. B. Chapman, D. J. Newman, J. Shorter, H. M. Wall, *J. Chem. Soc. Perkin Trans. 2* (1976) 847
10. J. G. Kirkwood, *J. Chem. Phys.* **2** (1934) 351
11. R. W. Taft, *Steric Effects in Organic Chemistry*, M. S. Newman, Wiley, New York, 1956, p. 13
12. R. M. Silverstein, G. C. Bassler, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1968, p. 68
13. M. H. Aslam, N. B. Chapman, J. Shorter, M. Charton, *J. Chem. Res.* (1980) 2301
14. M. Kamlet, J. Abboud, R. W. Taft, *Progress in Physical Organic Chemistry*, vol. 13 (1983) 485
15. Y. Marcus, *Chem. Soc. Rev.* (1983) 409
16. L. I. Smith, K. L. Howard, *Org. Synth., Coll., Vol. III* (1955) 351
17. A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, H. M. Wall., *J. Chem. Soc. B* (1968) 631
18. J. D. Roberts, E. A. McElhill, R. Armstrong, *J. Am. Chem. Soc.* **71** (1949) 2923.