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Investigations of the reactivity of pyridine carboxylic acids with diazodiphenylmethane in protic and aprotic solvents. Part I. Pyridine mono-carboxylic acids

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Abstract: Rate constants for the reaction of diazodiphenylmethane with isomeric pyridine carboxylic acids were determined in chosen protic and aprotic solvents at 30 °C, using the well known UV spectrophotometric method. The values of the rate constants of the investigated acids in protic solvents were higher than those in aprotic solvents. The second order rate constants were correlated with solvent parameters using the Kamlet-Taft solvatochromic equation in the form: $\log k = \log k_0 + s\pi^* + a\alpha + b\beta$. The correlation of the obtained kinetic data were performed by means of multiple linear regression analysis taking appropriate solvent parameters. The signs of the equation coefficients were in agreement with the postulated reaction mechanism. The mode of the influence of the solvent on the reaction rate in all the investigated acids are discussed on the basis of the correlation results.

Keywords: pyridine carboxylic acids, diazodiphenylmethane, rate constants, solvent parameters, protic and aprotic solvents.

INTRODUCTION

The relationship between the structure of carboxylic acids and their reactivity with diazodiphenylmethane (DDM) has been studied by many authors,[1,2] with particular regard to the influence of the solvent. The reaction between carboxylic acids and DDM may vary in rate, but takes place without any additional support and in aprotic solvents it follows second order kinetics.[3,4] In the present work the rate constants for isomeric pyridine mono-carboxylic acids were determined in twenty aprotic solvents and the previously obtained results for the reaction in eleven alcohols[5] have been included in this paper. The solvent effects on reaction rate constants were interpreted by means of the linear solvation energy relationship (LSER) concept, developed by Kamlet and Taft[6] expressed in the next form:

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$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

where α, β and π^* are solvent parameters and s, a and b are solvatochromic coefficients.

The parameter π^* is an 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 parameter represents the solvent hydrogen bond donor (HBD) acidity, which is the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The α values were selected to extend from zero for non-HBD solvents (*e.g.*, *n*-hexane) to about 1.00 for methanol. The β parameter is a measure of hydrogen bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton (or, *vice versa*, to donate an electron pair) in a solvent-to-solute hydrogen bond. The β values were selected to extend from 0.00 for non-HBA solvents (*e.g.*, *n*-hexane) to about 1.00 for hexamethylphosphoric acid triamide (HMPT).

RESULTS AND DISCUSSION

The kinetic study of the investigated acids and the explanation of the differences in the influence of protic and aprotic solvents on the reaction rates of pyridine mono-carboxylic acids with DDM were the objectives of this work. Comparison with kinetic data for benzoic acid under the same reaction condition, and comparative analysis of the reactivity of investigated acids are included in the explanation of the significance of the presence and position of the pyridine nitrogen.

The mechanism of the reaction between carboxylic acids and DDM has been thoroughly studied by Roberts,[3] Bowden,[7] Chapman,[8–18] and a spectrophotometric method and kinetic approaches have been developed. The influence of protic solvents on the reaction involving isomeric pyridine and the corresponding N-oxide carboxylic acid,[5] 6-substituted pyridine carboxylic acid,[19] isomeric 3- and 4-pyridineacetic acid and N-oxide derivatives[20] in their reaction with DDM has been thoroughly investigated. No similar study has, so far, been exclusively devoted to pyridine carboxylic acids in aprotic solvents.

The mechanism of the reaction in both protic and aprotic solvents was found to involve the rate-determining proton transfer from the acid to DDM forming a diphenylmethanediazonium carboxylate ion-pair.[12,13,16,21,22]

$$Ph_2CN_2 + RCOOH \xrightarrow{\text{slow}} Ph_2CHN_2^+ - OOCR \quad (2)$$

Rate constants for all three isomeric pyridine mono-carboxylic acids determined in the present study are given in Table I, together with the results of a previous study of these acids in protic solvents.[5]

The results show (Table I) that the rate constants increase with increasing polarity of the solvent. Comparison of the reaction constants in protic and aprotic solvents indicates that the reaction is slower in aprotic than in protic solvents, which is

TABLE I. Rate constants ($dm^3mol^{-1}min^{-1}$) for the reaction of nicotinic, isonicotinic and picolinic acids with DDM in protic and aprotic solvents at 30 °C

Solvent	Nicotinic		Isonicotinic		Picolinic	
	k_2	log k_2	k_2	log k_2	k_2	log k_2
Methanol**	10.70	1.029	20.20	1.305	10.96	1.040
Ethanol**	5.40	0.732	12.0	1.076	7.30	0.863
Propan-1-ol**	6.20	0.790	7.50	0.873	6.40	0.806
Propan-2-ol**	4.40	0.643	6.38	0.805	4.80	0.680
2-Methylpropan-2-ol**	1.70	0.223	2.97	0.473	1.33	0.124
2-Methypropan-1-ol**	6.97	0.843	12.07	1.081	8.73	0.941
Butan-1-ol**	4.77	0.678	6.40	0.806	5.54	0.744
Butan-2-ol**	3.45	0.538	5.72	0.757	4.19	0.622
2-Methybutan-2-ol**	1.26	0.100	1.91	0.281	0.86	–0.065
Pentan-1-ol**	3.72	0.571	7.32	0.865	4.10	0.613
Benzyl alcohol**	26.53	1.424	42.94	1.633	28.06	1.448
Ethylene glycol	35.10	1.545	–*	–	27.34	1.437
Dimethyl sulfoxide	0.21	–0.678	0.35	–0.456	0.10	–1.000
N,*N*-dimethylacetamide	0.12	–0.939	0.21	–0.670	0.04	–1.400
1-Methyl-2-pyrrolidone	0.12	–0.921	0.22	–0.656	0.037	–1.430
N,*N*-Dimethylformamide	0.25	–0.611	0.44	–0.354	0.098	–1.010
Acetophenone	5.17	0.714	1.69	0.229	1.36	0.135
2-Pyrrolidinone	0.15	–0.824	0.11	–0.961	0.14	–0.850
Sulfolan	14.79	1.170	–	–	3.97	0.599
N-Methylformamide	0.94	–0.027	1.12	0.050	1.35	0.130
Butan-2-one	2.51	0.400	1.49	0.172	0.19	–0.713
Acetone	1.56	0.190	3.52	0.546	0.19	–0.701
Chloroform	40.36	1.606	–	–	13.24	1.122
Ethyl benzoate	3.37	0.528	–	–	6.25	0.796
Acetonitrile	12.80	1.107	–	–	1.76	0.247
Diethyl carbonate	–	–	–	–	0.049	–1.309
Methyl acetate	1.39	0.144	–	–	0.88	–0.052
Butyl acetate	0.72	–0.145	–	–	0.16	–0.788
4-Methylpentan-2-one	1.39	0.143	0.98	–0.0075	0.21	–0.671
Ethyl acetate	1.22	0.085	0.88	–0.052	0.16	–0.788
Tetrahydrofuran	1.83	0.262	0.30	–0.523	–	–
Dioxane	0.24	–0.620	0.58	–0.237	–	–

* not soluble; ** Ref. 5

in accordance with the proposed mechanism of the reaction. The results of the kinetic studies show that reaction rates for all three acids with DDM were of second order, which was confirmed by the high correlation coefficients *r*, which were in the range 0.95 – 0.99 for both series of solvents.

Kamlet *et al.*[6] established that the effect of a solvent on the reaction rate should be given in terms of the following properties: (*i*) the behaviour of the solvent as a dielectric, facilitating the separation of opposite charges in the transition state (*ii*) the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond and thus stabilize the carboxylate anion in the transition state (*iii*) the ability of the solvent to stabilize the proton of the initial carboxylic acid by donating an ion pair. The parameter π^* is a quite suitable measure of the first property, while the second and third properties are governed by the effects of solvent acidity and basicity, expressed quantitatively by the parameters α and β.

The results of multiple linear regression correlation for isomeric pyridine carboxylic acids have been compared to the results for benzoic acid, and, finally, an overall comparison has been made for all the investigated acids. The discussion is based on the quantitative values and the sign of the coefficients in the corresponding equations and, finally, the comparison of these coefficients between themselves. An interesting observation for all the investigated acids are the possible modes of the influence of the solvent on the reactivity of the investigated acids, acting on two sites in the initial (Fig. 1) and in the transition states (Eq. (2)), of the pyridine carboxylic acids molecules, which are presented in Fig. 1.

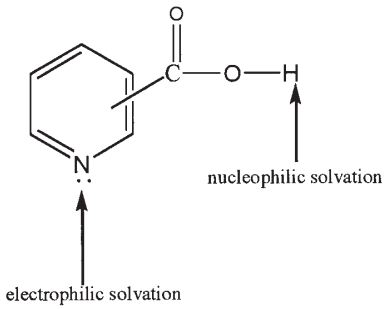


Fig. 1. The mode of the solvent effects in pyridine mono-carboxylic acids.

The effect of the electrophilic solvation of the pyridine nitrogen cannot be neglected, particularly for protic solvents, and for those aprotic solvents which possess partially acidic character ($\alpha \neq 0$). The effect of electrophilic solvation of nitrogen in the transition state is also included in the discussion which follows. The overall effect of a solvent on the reaction rate, which includes the previously quoted modes of the influence of the solvent have been discussed but a clearer separation of these influences on the molecules of pyridine mono-carboxylic acids as a whole cannot be drawn on the basis of the presented results. This means that electrophilic solvation does not uniquely affect the reaction rate in the transition state of

the reaction. Instead of this, the effect can be noticed as electrophilic solvation in the initial state, which contributes to the overall value of the coefficient *a*. The same observation holds for classical solvation and nucleophilic solvation but these effects are less complicated than those of electrophilic solvation.

The protic solvents

The kinetic data for nicotinic acid from Table I were correlated with the solvent parameters[23,24] for protic solvents, giving the following results:

$$\log k_2 = (-0.14 \pm 0.94) + (1.34 \pm 0.52)\,\pi^* + (0.78 \pm 0.21)\,\alpha + (-0.51 \pm 0.76)\,\beta \quad (3)$$
$$R = 0.960 \quad SD = 0.12 \quad n = 11$$

All the coefficients are in agreement with the mechanism of this reaction but all of them are not statistically correct. The negative value of the coefficient *b* indicates that nucleophilic solvation decreases the reaction rate, which corroborates the established reaction mechanism but this parameter is disputable, making the three-parameters equation useless for the interpretation of the kinetic data, because of the statistical deficiency of the parameters. Also, three parameter correlations for isonicotinic and picolinic acids for protic solvents were unacceptable for further analysis.

Therefore, the best interpretation of the solvent effects for protic solvents are described by the system of a simplified two-parameters equation of the following type:

$$\log k_2 = (-0.76 \pm 0.165) + (1.65 \pm 0.22)\,\pi^* + (0.85 \pm 0.16)\,\alpha \quad (4)$$
$$R = 0.960 \quad SD = 0.109 \quad n = 11$$

The results of the above correlations corroborate the reaction mechanism, and the influence of the solvent by the effect of classic solvation and electrophilic solvation. It is evident that HBD effect inceases the reaction rate, stabilizing the transition state more than the initial state, resulting in the positive signs of the coefficients *s* and *a*.

Comparison of the above correlations for nicotinic acid with the identical ones for benzoic acid (Eq. (5)), using values of the kinetic data from the literature,[25]

$$\log k_2 = -2.87 + (-0.83 \pm 0.36)\,\pi^* + (3.20 \pm 0.73)\,\alpha \quad (5)$$
$$R = 0.975 \quad SD = 0.103 \quad n = 7$$

by calculating the percentage contribution[26] of the individual solvent effects indicates that the significance of the classic solvation effect (π^*) is 66 % and the HBD effect (α) is 34 % for nicotinic acid, while for benzoic acid the effect of electrophilic solvation is the main effect (20.6 % and 79.4 %, respectively). The large differences in the contributions of the individual solvent effects for these two acids can be explained by a significant increase of the influence of classical solvation because of the more polarizable structure of nicotinic acid in the transition state, caused by the negative inductive and resonance effects of the pyridine nitrogen.

The same procedure was performed for isonicotinic acid:

$$\log k_2 = (-0.58 \pm 0.19) + (1.65 \pm 0.25)\,\pi^* + (0.90 \pm 0.21)\,\alpha \qquad (6)$$
$$R = 0.943 \quad SD = 0.14 \quad n = 11$$

Analysis of Eq. (6) leads to the conclusions: the high positive value of the coefficient *s* indicates that the effect of classic solvation of the transition state is the main solvent effect which influences the reactivity of this acid. The transition state is better stabilized than the initial state causing a more polar solvent to increase the reaction rate. According to the smaller positive value of the coefficient *a*, electrophilic solvation of the transition state is less pronounced than classic solvation, which also increases the reaction rate.

The small decrease of the value of percentage contribution of the coefficient *s* for isonicotinic acid, which is 58 % compared to the value for nicotinic 66 %, can be explained by better solvation of the more dipolar structure of the nicotinic acid–DDM adduct in the transition state. Electrophilic solvation is more pronounced for isonicotinic acid than for nicotinic, while the largest effect is for benzoic acid.

The correlation of the log *k* values for picolinic acid determined in protic solvents with the corresponding parameters π^* and α gave the following result:

$$\log k_2 = (-2.87 \pm 0.21) + (1.68 \pm 0.27)\,\pi^* + (1.17 \pm 0.22)\,\alpha \qquad (7)$$
$$R = 0.960 \quad SD = 0.14 \quad n = 7$$

Analysis of the above equations led to the following conclusions:

Classical solvation is the dominant factor influencing the reaction rate and the positive sign of the coefficient *s* indicates a better solvation of the transition state compared to that in the initial state. The high positive value of the coefficient *a* indicates a strong stabilization of the transition state by the HBD solvent effect, indicating stabilization of the formation of the carboxylate anion. The percentage contributions of the particular solvent effects for picolinic acid are: $\pi^* = 59$ %, $\alpha = 41$ %.

A summary of the results for all the examined acids in protic solvents is given in Table II.

TABLE II. The percentage contributions of the protic solvent effects (%)

Coefficient (parameter)	*s* (π^*)	*a* (α)
Benzoic acid	20.6	79.4
Nicotinic acid	66.0	34.0
Isonicotinic acid	58.0	42.0
Picolinic acid	59.0	41.0

Benzoic acid appears to have the highest contribution of electrophilic solvation in the transition state. According to this result, it follows that the stabilization of the negative charge at the pyridine nitrogen by the HBD solvent effect increases

the stabilization of the carboxylate anion, but decreases the reaction rate. It is evident that this stabilization decreases the nucleophilicity of the carboxylate anion for attack at the diazodiphenylmethane carbocation. Classical solvation is a more important solvent effect for all the isomeric pyridine carboxylic acids because of the more polarizable structure of these acids, where this effect is the most pronounced for nicotinic acid because of the impossibility of direct resonance interaction of the pyridine nitrogen with the carboxylic group.

The aprotic solvents

The same approach as for protic solvents was used for the kinetic data of nicotinic acid in approtic solvents (Table I), with tetrahydrofuran, butyl acetate and ethyl acetate excluded:

$$\log k_2 = (0.13 \pm 0.38) + (3.22 \pm 0.64)\pi^* + (1.53 \pm 0.41)\alpha + (-5.14 \pm 0.48)\beta \quad (8)$$
$$R = 0.955 \quad SD = 0.264 \quad n = 16$$

The above result indicates that the influence of the solvent on the rate is mainly the result of the strong basic character of aprotic solvent molecules, which is reflected in the high values of the coefficient *b* (Table III). Nucleophilic solvation, the basicity of an aprotic solvent, is the main solvent effect which affects the decrease of the reaction rate of the reaction of the investigated acid. The percentage contributions of the individual solvent effects for nicotinic acid is 33 % classical solvation, 15 % electrophilic solvation and 52 % nucleophilic solvation. In this case, also, the HBD solvent effect and classical solvation increase the reaction rate.

One correlation was found in the literature[27] which includes all three solvent parameters in the correlation for benzoic acid in solvents which allegedly do not possess HBD character:

$$\log k_2 = 0.20 + 1.21\,\pi^* + 2.71\,\alpha - 3.70\,\beta \quad (9)$$
$$R = 0.980 \quad SD = 0.171 \quad n = 44$$

The percentage contributions of the individual solvent effects calculated from the above Eq. (9) are: $\pi^* = 16$ %; $\alpha = 35$ %; $\beta = 49$ %. A comparative study of these results (Eq. (9)) with those for nicotinic acid (Eq. (8)) leads to the conclusion that classical solvation is more important for nicotinic acid, while electrophilic stabilization, *i.e.*, the HBD solvent effect, is more important for benzoic acid. For both acids, the basicity of an aprotic solvent, or the nucleophilic stabilization of the initial state of the molecules, which decreases the reaction rate, is the main factor affecting their reactivity. This effect is more pronounced in the correlation for nicotinic acid because of its higher acidity.

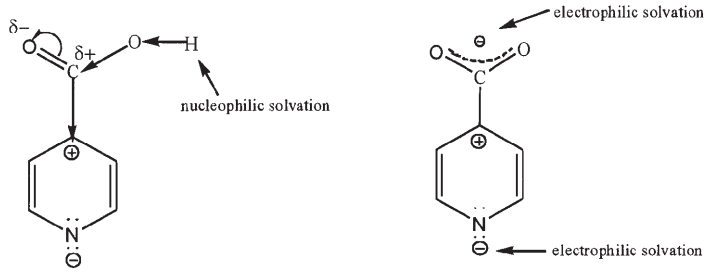
The suprisingly high values of the coefficient *a* for aprotic solvents in the two previous equations, especially the one for benzoic acid, indicate the important role of the HBD effect of aprotic solvents, which increases the reaction rate by stabilizing the acid anion.

The correlation of the log k values for isonicotinic acid with the parameters π^*, α and β for aprotic solvents gave the following results:

$$\log k_2 = (0.075 \pm 0.22) + (1.67 \pm 0.43)\pi^* + (1.26 \pm 0.23)\alpha + (-2.87 \pm 0.47)\beta \quad (10)$$
$$R = 0.953 \quad SD = 0.123 \quad n = 9$$

Classical and electrophilic solvation increase the reaction rate of this acid, while nucleophilic solvation of the initial state decreases the reaction rate. The percentage contributions of the individual solvent parameters are: 29 % for classical solvation, 21 % for electrophilic solvation and 50 % for nucleophilic solvation (Table III).

Although a better solvation of the carboxylic group proton of isonicotinic acid in the initial state was expected because it is more acidic than nicotinic acid, there is small difference between the values of the contribution of coefficient b for isonicotinic and nicotinic acids, due to negative inductive and resonance effects, which are presented in Fig. 2a.



a) b)

Fig. 2. Favourable mesomeric structures of isonicotinic acid and isonicotinic acid carboxylate anion.

The kinetic data for nicotinic and isonicotinic acids in aprotic solvents (Table I) show interesting results as the rate constants strongly depend on the effects of aprotic solvents which is reflected in the value of coefficient b. The higher value of electrophilic solvation in the transition state for isonicotinic acid can be explained by the joint effect of solvation of either the forming carboxylate anion or the partial negative charge on the nitrogen of the pyridyl group (Fig. 2b). The better classical solvation of nicotinic acid (Fig. 3b) is caused, probably, by a less pronounced direct resonance interaction than in isonicotinic acid (Fig. 2b), leading to a more polarizable structure resulting in better solvation by the dipolar solvent effect.

The correlation of the log k values for picolinic acid with the parameters π^*, α, and β for aprotic solvents gave the following results:

$$\log k_2 = (-0.46\pm0.26)+(2.80\pm0.43)\pi^*+(2.27\pm0.37)\alpha+(-4.44\pm0.41)\beta \quad (11)$$
$$R = 0.956 \quad SD = 0.24 \quad n = 17$$

The high negative value of the coefficient *b* shows that solvation by the HBA solvent effect, namely the nucleophilic solvation of the initial state, is a more important effect then the other two. The positive signs of the coefficients *s* and *a* indicate significant classical and electrophilic solvation, but they are of less significance than nucleophilic solvation. The calculations of the percentage contributions of the partial solvent effect gave the following results: $\pi^* = 29$ %; $\alpha = 24$ %; $\beta = 47$ %.

The overall comparison of the results of solvent effects on the reactivity of pyridine carboxylic acids is presented in Table III.

TABLE III. The percentage contributions of the aprotic solvent effects (%)

Coefficient (parameter)	*s* (π^*)	*a* (α)	*b* (β)
Nicotinic acid	33	15	52
Isonicotinic acid	29	21	50
Picolinic acid	29	24	47
Benzoic acid	16	35	49

The data from Table III indicate that the HBD solvent effect (acidity) significantly affects the stabilization of the transition state, and that this solvent effect is more important for picolinic than for isonicotinic and nicotinic acids. The higher value of the parameter which expresses the effect of electrophilic solvation for picolinic acid, can, most probably, be explained in the following way: the carboxylate anion forming in the transition state is very close to the pyridine nitrogen, causing, to some extent, a repulsion between the identical negative charges, resulting in the planar carboxylate anion being in a perpendicular position with respect to the pyridine ring, which is therefore subjected to a better electrophilic solvation (Fig. 3a). As can be seen, the highest value of the HBD effect for benzoic acid is most probably influenced by the exclusive stabilization of the carboxylate ion, with no stabilization of the negative charge on the pyridine nitrogen, as is the case for the isomeric pyridine carboxylic acids.

Classical solvation (π^*) is more pronounced for nicotinic acid because its molecule has a more distinct dipolar structure than the molecule of the other two investigated pyridine mono-carboxylic acids, as is presented in Fig. 3b.

a) b)

Fig. 3. Carboxylate anions of picolinic and nicotinic acid. a) Favourable geometry of the picolinic acid carboxylate anion. b) More extensive polarization of the nicotinic acid carboxylate anion.

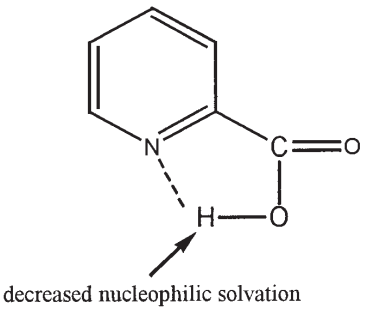


Fig. 4. Weak intramolecular hydrogen bond in picolinic acid.

The percentage contribution of the HBA solvent effect shows a small decrease for picolinic acid. This can be explained, probably, by the ability of picolinic acid to create a weak intramolecular hydrogen bond in the initial state, as is shown in Fig. 4, which decreases the influence of solvents.

It is well known from a previous kinetic study[28] that the reactivity of the carboxylic group in the investigated series of acids is highly dependent on its position with respect to the pyridine nitrogen. The overall solvent effects on reactivity, which are the subject of the present study, are further complicated by the possibility of direct conjugation in isonicotinic and picolinic acids, as well as by steric effects and the existence of a moderate strength intramolecular hydrogen bond in the initial state of picolinic acid. Therefore there are several possible modes of interactions of a solvent, either protic or aprotic, with more active sites of the reacting acid molecules. The results of the present investigations show that the diverse solvent effects could, generally, be quantified by use of the Kamlet–Taft equation, but the quantitative separation of these solvent effects into individual contributions in the transition and initial states by applying a mathematical treatment is not completely possible in this study, due to the diversity of particular polar groups and their position in the investigated molecules.

ИЗВОД

ИСПИТИВАЊЕ РЕАКТИВНОСТИ ПИРИДИН–МОНОКАРБОНСКИХ КИСЕЛИНА У РЕАКЦИЈИ СА ДИАЗОДИФЕНИЛМЕТАНОМ У ПРОТИЧНИМ И АПРОТИЧНИМ РАСТВАРАЧИМА. ДЕО I

АЛЕКСАНДАР Д. МАРИНКОВИЋ, САША Ж. ДРМАНИЋ, БРАТИСЛАВ Ж. ЈОВАНОВИЋ и МИЛИЦА МИШИЋ-ВУКОВИЋ

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Константе брзина реакције између диазодифенилметана и изомерних пиридин-карбонских киселина су одређене у одабраним протичним и апротичним растварачима на 30 °C, коришћењем познате УВ спектрофотометријске методе. Вредности константи брзина испитиване реакције у протичним растварачима имају веће вредности у поређењу са вредностима константи у апротичним растваражима. Константе брзина су корелисане са параметрима растварача коришћењем Kamlet–Taft једначине облика:

$\log k = \log k_0 + s\pi^* + a\alpha + b\beta$**.** Корелације добијених кинетичких резултата са одговарајућим параметрима растварача су изведене методом вишеструке линеарне регресионе анализе. Знак коефицијената у добијеним корелацијама је у сагласности са претпостављеним реакционим механизмом. Утицај растварача на вредности реакционих константи је дискутован на основу добијених корелационих резултата.

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