A comparative LFER study of the reactivity of pyridineacetic, pyridineacetic acids *N*-oxide and substituted phenylacetic acids with diazodiphenylmethane in various alcohols

SAŠA Ž. DRMANIĆ, BRATISLAV Ž. JOVANOVIĆ[#] and MILICA M. MIŠIĆ-VUKOVIĆ[#]

Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P. O. Box 35-03, YU-11001 Belgrade, Yugoslavia

Rate constants have been determined for the reactions of diazodiphenylmethane (DDM) with 3- and 4-pyridineacetic acid, 3- and 4-pyridineacetic acid *N*-oxide and some *meta*- and *para*-substituted phenylacetic acids in twelve alcohols. The determined rate constants, together with literature data, were used for calculation of Hammett ρ values in a series of alcohols. Secondary σ constants have been calculated for substituents in *meta* and *para*-position of phenylacetic acids not given in literature, and also σ constants for 3N, 3N–O, 4N and 4N–O in pyridineacetic acids, in alcohols used. The transmission of electronic effects through the phenylacetic acid system and pyridineacetic system is compared with that in benzene and pyridine. The multiple correlation of log *k* values for reaction of above acids in 12 alcohols with group of suitable solvent parameters was very successful.

Keywords: substituted pyridineacetic and phenylacetic acids, protic solvents, solvent parameters, Hammett correlation.

INTRODUCTION

In connection with our study of the transmission of substituent effects in *meta*- and *para*-position through pyridine ring and benzene ring, we now in this paper extend our previous work[1,2] on the reactivity of *meta*- and *para*-substituted phenylacetic acids and 3- and 4-pyridineacetic acid and 3- and 4-pyridineacetic acid *N*-oxide in the same alcohols. Other autors[3] investigated the reactivity of certain 3- and 4-substituted phenylacetic acids in a similar solvent system.[3] We studied the kinetics of the reactions of *para*- and *meta*-substituted phenylacetic acids with substituents: H, Cl, CH₃, NO₂, OH, 3- and 4-pyridineacetic acids and 3- and 4-pyridineacetic acids *N*-oxides in a series of alcohols to elucidate the influence of solvents on the rate, σ constants and also on the reaction constants ρ. Obtained results are compared with the data for the *meta*- and *para*-substituted benzoic acids with the same substituents and also for pyridine carboxylic acids.[1,2]

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DRMANIĆ, JOVANOVIĆ and MIŠIĆ-VUKOVIĆ

RESULTS AND DISCUSSION

The mechanism of the reaction between carboxylic acids and DDM has been throughly studied,[4–7] and found to involve rate-determining proton transfer from the acids to DDM to form a diphenylmethanediazonium carboxylate ion-pair.[5,8,9]

$$Ph_2CN_2 + RCOOH \xrightarrow{\text{slow}} Ph_2CHN_2^+ \, \overline{O}OCR$$
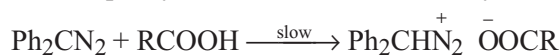
The rate data for the reaction with DDM in alcohols obtained in the present study together with literature data for investigated acids, are given in Tables I and II.

TABLE I. Rate constants ($dm^3 \, mol^{-1} \, min^{-1}$) for the reaction of *meta*-substituted phenylacetic acids, 3-pyridineacetic acid and 3-pyridineacetic acid *N*-oxide with DDM at 30 ºC in various alcohols

Solvent	H	3–Cl	3–NO$_2$	3–CH$_3$	3–OH	3N	3N–O
Methanol	2.54[a]	3.45[a]	4.49[a]	2.49[a]	2.6	5.06	9.1
Ethanol	1.14[a]	1.65[a]	2.25[a]	1.12[a]	1.2	2.35	4.9
Propan-1-ol	1.32[a]	1.88[a]	2.63[a]	1.27[a]	1.34	3.07	4.9
Butan-1-ol	1.18[a]	1.65	2.20	1.12	1.23	2.30	4.7
Propan-2-ol	0.808[a]	1.25[a]	1.79[a]	0.787[a]	0.80	1.94	3.53
Butan-2-ol	0.825[a]	1.32	1.75	0.76	0.83	1.82	3.42
Cyclopentanol	0.980	1.45	2.11	0.95	0.01	2.21	3.8
2-Me-butan-2-ol	0.192[a]	0.355[a]	0.663[a]	0.176[a]	0.24	0.579	1.14
Pentan-1-ol	1.24	1.65	2.51	1.04	1.1	2.57	4.3
2-Me-propan-1-ol	1.95[a]	2.81[a]	3.96[a]	1.87[a]	2.04	4.04	6.97
2-Me-propan-2-ol	0.345[a]	0.594[a]	0.99[a]	0.319[a]	0.36	0.883	1.66
Benzyl alcohol	9.85[a]	13.2[a]	17.1[a]	9.50[a]	9.2	17.92	25.12

[a]Ref. 3

TABLE II. Rate constants ($dm^3 \, mol^{-1} \, min^{-1}$) for the reaction of *para*-substituted phenylacetic acids, 4-pyridineacetic acid, 4-pyridineacetic acid *N*-oxide with DDM at 30 ºC in various alcohols

Solvent	H	4Cl	4NO$_2$	4CH$_3$	4OH	4N	4N–O
Methanol	2.54[a]	3.04[a]	4.47[a]	2.36[a]	2.2	5.5	6.8
Ethanol	1.14[a]	1.42[a]	2.21[a]	1.05[a]	0.94	3.04	4.3
Propan-1-ol	1.32[a]	1.83	2.63[a]	1.21	1.05	3.1	4.1
Butan-1-ol	1.18[a]	1.59	2.33	1.08	0.95	2.35	3.6
Propan-2-ol	0.808[a]	1.11[a]	1.78[a]	0.736[a]	0.68	2.2	3.2
Butan-2-ol	0.825[a]	1.26	2.12	0.74	0.67	1.9	2.9
Cyclopentanol	0.980	1.38	2.19	0.87	0.78	2.3	2.9
2-Me-butan-2-ol	0.192[a]	0.320[a]	0.722[a]	0.165[a]	0.14	0.61	0.98
Pentan-1-ol	1.24	1.59	2.51	0.96	0.92	2.7	3.4
2-Me-propan-1-ol	1.95[a]	2.50[a]	3.91[a]	1.81	1.66	–	6.44
2-Me-propan-2-ol	0.345[a]	0.532[a]	1.02[a]	0.309[a]	0.273	–	1.41
Benzyl alcohol	9.85[a]	11.75	18.5[a]	8.6	8.1	–	21.3

[a]Ref. 3

The literature data for substituted benzoic acids used in this work are taken from literature.[1,2,5,10,11] The reactivity of unstable 4-pyridineacetic acid[12] was studied under specific conditions. Namely, this acid which decomposes at reaction conditions was investigated *via* its hydrochloride[13] which was neutralized *in situ*. This method is described in the experimental section.

The log k values of the investigated acids in all alcohol solvents used, show a linear correlation with the corresponding values of log k for the reaction of benzoic acid with DDM at 30 ºC in the same solvents taken from the literature,[5,10,11] with correlation coefficient r in the range (0.97 – 0.99) and standard deviation s (0.01 – 0.07), except for 4-pyridineacetic acid ($r = 0.93$), ($s = 0.129$). Such linear free-energy intercorrelations indicate that the same solvent properties influence the reactivity of benzoic acid and the investigated acids.

Solvent effects on the rate constants for the reaction of investigated acids with DDM

Since the mechanism of the reaction involves the formation of an ion-pair intermediate one may expect the rate to increase with an increase in the polarity of the solvent.[14]

The attempted correlation between the rates and dielectric constant ε, or $1/\varepsilon$ or the Kirkwood function[15] of dielectric constant, $f(\varepsilon) = (\varepsilon_r - 1)/(2\varepsilon_r + 1)$ was poor. The correlation of log k with σ^*, the polar constant of the alkyl group[16] of the alcohol was satisfactory for p-supstituted phenylacetic acid ($r = 0.960$), for 3-pyridineacetic, 3- and 4-pyridineacetic acids N-oxide ($r = 0.970$), and for 4-pyridineacetic acid ($r = 0.925$).

Chapman *et al.*[17] and other autors[18] have established that the solvent effect is best interpreted and investigated by the equation

$$\log k = a + bf(\varepsilon) + c\sigma^* + dn_{\gamma H} \tag{1}$$

where the $f(\varepsilon)$ is Kirkwood function,[15] σ^* is Taft polar constants of alkyl group in alcohols[16] and $n_{\gamma H}$ is the number of γ-hydrogen atoms in alcohols. These solvent parameters for alcohols are given in the literature.[10]

Multiple linear regressions of the log k for the acids from Table I and II with $f(\varepsilon)$, σ^* and $n_{\gamma H}$ in alcohol solvents are given in the following equations:

3N-pyridineacetic acid:

$$\log k = (-0.380 \pm 0.413) + (2.357 \pm 0.8935)\, f(\varepsilon) + (2.531 \pm 0.1620)\, \sigma^* +$$
$$+ (0.029 \pm 0.011)\, n_{\gamma H} \tag{2}$$
$$(r = 0.9888;\ s = 0.065,\ n = 12)$$

3-Pyridineacetic acid N-oxide:

$$\log k = (-0.392 \pm 0.272) + (2.762 \pm 0.589)\, f(\varepsilon) + (2.257 \pm 0.107)\, \sigma^* +$$
$$+ (0.025 \pm 0.007)\, n_{\gamma H} \tag{3}$$
$$(r = 0.9941;\ s = 0.043,\ n = 12)$$

4-Pyridineacetic acid:

$$\log k = (-1.706 \pm 1.175) + (5.251 \pm 2.377)\, f(\varepsilon) + (1.892 \pm 0.782)\, \sigma^* +$$
$$+ (0.019 \pm 0.029)\, n_{\gamma H} \tag{4}$$
$$(r = 0.9635;\ s = 0.099,\ n = 9)$$

4-Pyridineacetic acid *N*-oxide:

$$\log k = (-0.376 \pm 0.3973) + (2.647 \pm 0.8581)\, f(\varepsilon) + (2.244 \pm 0.156)\, \sigma^* +$$
$$+ (0.03 \pm 0.010)\, n_{\gamma H} \tag{5}$$
$$(r = 0.9873;\ s = 0.063,\ n = 12)$$

After analyzing above equations and equations from literature[1,2,3] it could be said that influence of relative permittivity as a term of the Kirkwood function on the rate constants of benzoic and pyridine carboxylic acids is more important than in phenylacetic and pyridineacetic acids. The influence of the polarity of the solvent alkyl group, expressed by Taft polar constants σ^*, appears to be the main influence on the rate of chemical reaction in alcohols.[1,19] This is also confirmed in this work by good partial correlation with σ^* only, where the correlation coefficients are satisfactory, in contrast to separate correlation with other solvent parameters, $f(\varepsilon)$ and $n_{\gamma H}$, which were poor.

Influence of σ^* is of almost the same intensity for substituents in phenylacetic and pyridineacetic acid, and substituents in benzoic and pyridine carboxylic acids so that the differences in coefficients attached to σ^* for substituents in phenylacetic and pyridineacetic acids and substituents in benzoic and pyridine carboxylic acids are less than corresponding differences in coefficients attached to $f(\varepsilon)$. 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 alcohol.[19] The necessity to include it in this work was to account for the unexpectedly high values of rate constants for 2-methyl-propan-1-ol. The exclusion of $n_{\gamma H}$ gives poorer regression coefficients.

The variation of substituent σ constants with the solvent

In the course of the present work further information has been obtained on the solvent dependence of the σ values for 3N, 3N–O, 4N, 4N–O of pyridineacetic acids, *m*-OH, *p*-OH phenylacetic acids and *p*-NO$_2$, *p*-Cl and *p*-CH$_3$ phenylacetic acids in the solvents which have not been determined in the previous work.[3] Table III shows that the Hammett equation gives an excellent correlation for the *meta* substituted acids in each solvent. Hammett correlations were not successful for *p*-substituted acids,[3] whichever of the well known sets of σ-values is used, *viz*., σ (Jaffe),[20] σ^n (Wepster)[21] or σ^0 (Taft).[22]

In Table III literature values[3] of the reaction constant ρ and log k_0 for the reaction of a series of *m*-substituted phenylacetic acids with DDM are given, together with the data in the alcohols, butan-1-ol, butan-2-ol, pentan-1-ol and cyclopentanol determined in the present work. These values were used for the calculation of new secondary σ_m and σ_p constants by using Wepster's procedure.[21] The results obtained are collected in Table IV.

There are a substantial variety of the values of secondary σ constants in Table IV. This is understandable considering that the energy of the transition state has been influenced both by the solvent modified electronic effect of the substituent and by solvent effects on the stabilization of the initial *vs.* transition states.

It has been stated in literature[3] that *para*-substituents at phenylacetic acids as reflected by the corresponding secondary σ constants, irrespective of their polar nature, become more electron-attracting (or less electron-releasing) as the polarity of the solvent decreases. This is also true for the secondary σ_p constants determined in the present work and presented in Table IV together with literature data. On the contrary, secondary σ values for 4N and 4N–O in pyridineacetic acids show opposite behaviour, the same as it was for 4N and 4N–O in pyridine carboxylic acids from our previous work.[1] The possible explanation for the investigated heterocyclic nuclei is that the intermolecular hydrogen bonding between pyridine nitrogen and N-oxide function with alcohol hydroxylic group suppresses the electron donating ability of both groups, and this interaction is stronger with more polar alcohols.

Jaffe[20] and Chapman[3] have suggested that polar substituents may be extensively hydrogen-bonded to solvent molecules in hydroxylic media, and variation of substituent constants with the solvent is to be expected. Reaction in water and in aqueous mixtures play an important part in establishing σ-values and it seems certain that the influence of the specific solvation of substituents by water has often been incorporated in σ-values.[3]

TABLE III. Values of Hammett ρ and log k_0 values calculated for reaction of DDM with *meta* substituted phenylacetic acids (H, *m*–CH₃, *m*–Cl and *m*–NO₂) in various alcohols at 30 ºC

Solvent	ρ	log k_0	r^a
Methanol	0.34[b]	0.412	0.999
Ethanol	0.40[b]	0.068	0.998
Propan-1-ol	0.42[b]	0.125	0.999
Butan-1-ol	0.38	0.074	0.999
Propan-2-ol	0.47[b]	−0.081	0.999
Butan-2-ol	0.47	−0.079	0.995
Cyclopentanol	0.45	−0.001	0.999
2-Me-butan-2-ol	0.74[b]	−0.714	0.999
Pentan-1-ol	0.46	0.066	0.991
2-Me-propan-1-ol	0.42[b]	0.295	0.999
2-Me-propan-2-ol	0.63[b]	−0.458	1.000
Benzyl alcohol	0.33[b]	0.997	1.000

Footnotes: [a]Correlation coefficients, [b]Ref. 3

The σ_m values for OH are very close to zero, except for 2-methyl-2-butanol and benzyl alcohol, but the average value is in agreement to values previously determined for σ_m OH based on the reaction ionization of 3-hydroxy benzoic acid,[20] and from vari-

ous reactions where the average value of σ_m OH was –0.002.[19] In alcohols, the values range from –0.1 to 0.13, *i.e.,* giving an average value of 0.01. The hydrogen bonding between the hydroxylic group substituent and alcohol hydroxylic group has been extensively discussed in our previous paper[1] and also in literature.[19]

TABLE IV: Secondary values of σ_m for OH, 3N, 3N–O and σ_p for OH, CH$_3$, NO$_2$, Cl, 4N and 4N–O from reaction of substituted phenylacetic acids and substituted pyridineacetic with DDM in various alcohols

Solvent	OH	3N	3N–O	OH	CH$_3$	NO$_2$	Cl	4N	4N–O
	σ_m	σ_m	σ_m	σ_p	σ_p	σ_p	σ_p	σ_p	σ_p
Methanol	0.01	0.86	1.61	–0.21	–0.12[a]	0.71[a]	0.21[a]	0.97	1.24
Ethanol	0.02	0.76	1.56	–0.24	–0.11[a]	0.69[a]	0.21[a]	1.04	1.41
Propan-1-ol	0.005	0.82	1.34	–0.25	–0.10	0.70	0.33	0.87	1.16
Butan-1-ol	0.04	0.76	1.57	–0.25	–0.11	0.77	0.33	0.78	1.27
Propan-2-ol	–0.03	0.77	1.34	–0.18	–0.11[a]	0.70[a]	0.27[a]	0.90	1.25
Butan-2-ol	0.002	0.72	1.30	–0.20	–0.11	0.86	0.38	0.76	1.15
Cyclopentanol	0.01	0.77	1.29	–0.24	–0.13	0.75	0.31	0.81	1.03
2-Me-butan-2-ol	0.13	0.64	1.04	–0.19	–0.09[a]	0.77[a]	0.30[a]	0.68	0.95
Pentan-1-ol	–0.05	0.75	1.23	–0.23	–0.18	0.73	0.29	0.79	1.01
2-Me-propan-1-ol	0.04	0.74	1.30	–0.18	–0.09[a]	0.70[a]	0.24[a]	–	1.22
2-Me-propan-2-ol	0.02	0.64	1.08	–0.17	–0.08[a]	0.74[a]	0.29[a]	–	0.96
Benzyl alcohol	–0.10	0.78	1.22	–0.17	–0.08	0.74	0.29	–	1.01
Average values	0.01	0.75	1.32	–0.20	–0.11	0.74	0.28	0.84	1.14

[a]Ref. 3

Negative σ_p values for OH group are expected, considering the electron-donating effect through the direct influence, but in this system the electron donating effects of OH group is smaller than in benzene ring and this is understandable because of suppressed direct conjugation between the substituent and reaction center. The average value for σ_p OH constants, however, are in agreement with the constants from literature[20,22] and it may be stated that those σ_p OH constant could be satisfactory used for reactions in alcohol solvents.

It is interesting to note that the differences in σ_m in various solvents for 3N and 4N are smaller than for 3N–O and 4N–O group. This is not surprising as this is the most polarizable group in the whole range of substituents investigated here. These results also justify the calculation of secondary σ constants for the reaction in alcohols.

Solvent effects on calculated reaction constant ρ in the reactions of investigated acids with DDM

Using the average values of secondary σ_m, σ_p (Table IV) separate ρ_m for seven *meta-* and ρ_p for six *para*-substituted phenylacetic acids, were calculated in twelve investigated alcohols. These results are presented in Table V, and are lower than the values of reaction constants ρ for substituted benzoic acids.[1]

TABLE V: Values of reaction constants ρ and log k_0 for the reaction of DDM with *meta-* and *para-*substituted phenylacetic acids, 3-pyridineacetic, 3- and 4-pyridineacetic acids *N*-oxide in various alcohols at 30 ºC

Solvent	*m*-substituted acids H, 3N, 3N–O, 3–NO₂, 3–OH, 3–CH₃, 3–Cl				*p*-substituted acids H, 4N–O, 4–NO₂, 4–OH, 4–CH₃, 4–Cl			
	ρ_m	log k_0	*r*	*s*	ρ_p	log k_0	*r*	*s*
Methanol	0.400	0.404	0.9948	0.023	0.404	0.359	0.9961	0.019
Ethanol	0.451	0.06	0.9950	0.026	0.468	0.053	0.9891	0.041
Propan-1-ol	0.434	0.126	0.997	0.019	0.427	0.122	0.9979	0.016
Butan-1-ol	0.430	0.068	0.994	0.027	0.419	0.072	0.9989	0.012
Propan-2-ol	0.484	–0.086	0.999	0.012	0.494	–0.084	0.9969	0.023
Butan-2-ol	0.465	–0.08	0.998	0.014	0.491	–0.068	0.9954	0.028
Cyclopentanol	0.444	0.001	0.999	0.009	0.433	–0.006	0.9958	0.024
2-Me-butan-2-ol	0.587	–0.673	0.9875	0.053	0.660	–0.703	0.9919	0.050
Pentan-1-ol	0.446	0.062	0.996	0.024	0.430	0.062	0.9936	0.029
2-Me-propan-1-ol	0.413	0.30	0.999	0.006	0.432	0.295	0.9970	0.020
2-Me-propan-2-ol	0.53	–0.443	0.993	0.036	0.553	–0.446	0.9954	0.031
Benzyl alcohol	0.323	0.992	0.994	0.02	0.329	0.982	0.9906	0.027
Average values	0.451				0.465			

It was to be expected that the susceptibility to the polar effect of substituents will be greater for the substituted benzene ring than for substituted phenylacetic acid system, due to intervening methylene group. Calculated the average attenuating efect $\pi = \rho_{PhAA}/\rho_{BA} = 0.46$ is in very good agreement with literature values[13,17] for attenuating effects for *meta* and *para* substituted acids of similar structure where the values π are between 0.39 and 0.53.

The results given in the Table V shown that the ρ values are decreased by increasing the relative permittivity. This may be interpreted in two ways as have been suggested by some authors before.[20,23] Firstly, the transmission of the polar effects of the substitutents through the medium increases in importance relative to transmission through the molecular cavity as ε_r is decreased. Secondly, at high relative permittivities the energy necessary to bring about the charge separation in the transition state is relatively small, and this gives rise to a low susceptibility to the polar effects of substituents. The ρ values thus increases as the energy necessary to achieve charge separation increases as ε_r is decreased. Therefore it is reasonable to correlate ρ_m and ρ_p with solvent[10] parameters as was done for log k.

For the *para*-substituted phenylacetic acids and for *para*-substituted benzoic acids at 30 ºC from Table V, the following relationships were obtained for the corresponding series of acids in twelve alcohols:

– for *para*-substituted phenylacetic acids:

$$\rho_{p\text{PhAA}} = (1.093\pm0.193) - (1.506\pm0.416)\,f(\varepsilon) - (0.418\pm0.076)\,\sigma^* - \\ - (0.005\pm0.005)\,n_{\gamma\text{H}} \tag{6}$$
$$(r = 0.9504;\ s = 0.030;\ n = 12)$$

– for *para*-substituted benzoic acids:[1]

$$\rho_{p\text{BA}} = (1.665\pm0.281) - (1.670\pm0.608)\,f(\varepsilon) - (0.698\pm0.110)\,\sigma^* - \\ - (0.002\pm0.007)\,n_{\gamma\text{H}} \tag{7}$$
$$(r = 0.9531;\ s = 0.044;\ n = 12)$$

For the *meta*-substituted phenylacetic acids at 30 ºC from Table V and for *meta*-substituted benzoic acids,[1] the following relationships were obtained for the corresponding series of acids in twelve alcohols:

$$\rho_{m\text{PhAA}} = (0.793\pm0.095) - (0.854\pm0.204)\,f(\varepsilon) - (0.394\pm0.037)\,\sigma^* - \\ - (0.006\pm0.002)\,n_{\gamma\text{H}} \tag{8}$$
$$(r = 0.9810;\ s = 0.015;\ n = 12)$$

$$\rho_{m\text{BA}} = (1.308\pm0.306) - (0.960\pm0.661)\,f(\varepsilon) - (1.050\pm0.120)\,\sigma^* - \\ - (0.007\pm0.008)\,n_{\gamma\text{H}} \tag{9}$$
$$(r = 0.9658;\ s = 0.048;\ n = 12)$$

In our previous work[1] and some other papers[18,19] it has been suggested that the value associated with the σ^* term has a more significant contribution to ρ than the value associated with the $f(\varepsilon)$ term in alcohol solvents. The results obtained using multiple regression analysis with three solvent parameters, Eqs. (6–9), confirm the conclusions from our earlier paper[1] that σ^* in comparison with the dielectric term, had the main influence in the solvent effects.

The correlation coefficients in relationships (6–9) are not particularly high, but are better than those from two-parameter equations. This could have been expected, considering the large number of data involved in the overall calculation, and the possibility of direct resonance conjugation in *para*-substituted benzoic acids.

On the basis of all information presented, it may be concluded that linear free energy relationships are applicable to kinetic data for *meta*- and *para*-substituted phenylacetic, 3- and 4-pyridineacetic acids, and for 3- and 4-pyridineacetic acids *N*-oxide. The multiple linear correlations with three suitable solvent parameters $f(\varepsilon)$, σ^*, $n_{\gamma\text{H}}$ for both log k and ρ values were fairly successful.

EXPERIMENTAL

Materials

The acids were commercial samples or were prepared by standard methods. They were recrystallised, and had m.p.s. identical or very close to those recorded in the literature.

3-*Pyridineacetic acid N-oxide*, m.p. 140–142 ºC (Ref.24 142–144 ºC) was prepared by a known method and had the melting point as stated in Ref.24

4-*Pyridineacetic acid N-oxide*,[25] m.p. 143–144 ºC (dec.) (Ref.[25] 144–145 ºC) was prepared in rearrangement reaction from 4-(*N*-acetoacetyl)pyridinesulfonamide 1-oxide which is derived from 4-pyridinesulfonamide 1-oxide.[25]

Anal: Calcd. for $C_7H_7O_3N$: C, 54.91; H, 4.61. Found: C, 54.47; H, 4.38.

Diazodiphenylmethane was prepared by Smith and Howard's method,[26] 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 Ref. 1

All the solvents used for kinetic studies were examined by GLC and no impurities were detected.

Kinetic measurements

Rate constant *k*, for the reaction of investigated acids with DDM were determined as reported previously by the spectroscopic method of Roberts and his coworkers[27] 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 on each acid and in every case the individual second-order rate constants agreed within 3 % of the mean.

The solution of 4-pyridineacetic acid hydrochloride in investigated solvents was treated with KOH in the same solvents maintaining the same concentration as above, and immediately treated with DDM. However, precipitation of KCl interfered in the initial stage of the reaction and better results were obtained if the reaction was studied as a second order process.[13]

И З В О Д

КОМПАРАТИВНА LFER СТУДИЈА РЕАКТИВНОСТИ ПИРИДИНСИРЋЕТНИХ, ПИРИДИН-*N*-ОКСИД-СИРЋЕТНИХ КИСЕЛИНА И СУПСТИТУИСАНИХ ФЕНИЛСИРЋЕТНИХ КИСЕЛИНА СА ДИАЗОДИФЕНИЛМЕТАНОМ У РАЗЛИЧИТИМ АЛКОХОЛИМА

САША Ж. ДРМАНИЋ, БРАТИСЛАВ Ж. ЈОВАНОВИЋ и МИЛИЦА М. МИШИЋ-ВУКОВИЋ

Технолошко-мешалуршки факулшеш Универзишеша у Беоīраду, Карнеīијева 4, ū. ūр. 35-03, 11000 Беоīрад

Одређене су константе брзине реакције естерификације 3- и 4-пиридинсирћетне киселине, 3- и 4-пиридин-*N*-оксид-сирћетне киселине и неких *меша* и *ūара*-супституисаних фенилсирћетних киселина са диазодифенилметаном на 30 ºC у дванаест алкохолних растварача. На основу добијених константи брзина реакција пиридинсирћетних киселина и супституисаних фенилсирћетних киселина израчунате су нове секундарне σ константе супституената. Такође су коришћењем Hammett-ове једначине одређене реакционе константе ρ за наведене киселине и дискутован је ефекат пригушења метиленске групе. Вишеструком регресионом анализом успостављена је задовољавајћа зависност константи брзина реакција као и реакционе константе ρ са параметрима растварача као што су: Kirkwood-ова функција релативне пермитивности $f(\varepsilon)$, Тафтова σ^* константа за алкил групе алкохола и $n_{\gamma H}$ који представља број γ-водоникових атома у алкохолу.

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