

## The kinetics of the reaction of 6-substituted nicotinic acids and some *p*-substituted benzoic acids with diazodiphenylmethane in various alcohols

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Rate constants have been determined for the reactions of diazodiphenylmethane with a number of 6-substituted nicotinic acids and *p*-substituted benzoic acids in twelve alcohols. A comparative study was used to evaluate and compare the Hammett  $\rho$  values and solvent effects. Multiple correlations of the  $\log k$  values for the reactions of 6-substituted nicotinic acids and *p*-substituted benzoic acids in 12 alcohols with groups of suitable solvent parameters are very successful. The transmission of electronic effects through the pyridine ring system in compared with that in benzene.

*Keywords:* 6-substituted nicotinic acids, protic solvents, solvent parameters, Hammett correlation.

### INTRODUCTION

The transmission of electronic substituent effects through the pyridine nucleus has attracted little attention, particularly if the substituent is *ortho* to the nitrogen and *para* to the carboxylic acid reaction centre. Imoto *et al.*<sup>1</sup> have determined the dissociation constants of 6-substituted nicotinic acids (Cl, H, CH<sub>3</sub> and NO<sub>2</sub>) and obtained a successful Hammett correlation with  $\sigma_p$  constants ( $\rho = 0.16$ ). On the other hand, Campbell and coworkers,<sup>2</sup> on the basis of the rate constants for the alkaline hydrolysis of 6-substituted alkyl nicotines, concluded that the pyridine nucleus interfere with the transmission of substituent effects, particularly if electron-donor substituents were involved (OCH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>). Namely, the  $\log k_2$  values for these model substances deviated from LFER.

With the intention of clarifying this situation and using new data, in the present work, the reactivities of 6-substituted nicotinic acids to esterification with DDM in twelve protic solvents were investigated for the acids whose rate constants were not determined in our previous paper.<sup>3</sup> A comparative study of the available kinetic data on these acids (Table I) in twelve protic solvents was performed, using multiple

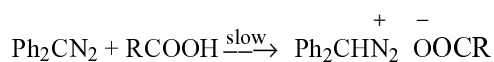
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correlation. The results of these calculations were compared with the corresponding substituent and solvent effects on the reactivity of *p*-substituted benzoic acids.<sup>3</sup>

The reaction of carboxylic acids with diazodiphenylmethane has been extensively studied by Roberts,<sup>4</sup> Chapman *et al.*,<sup>5-16</sup> as well as by other groups, who developed spectrophotometric methods and kinetic approaches for this type of investigation. Although the influence of solvents on the reaction involving benzoic acids,<sup>10</sup> phenylacetic acids,<sup>12</sup> *trans*-cinnamic acids<sup>15</sup> has been thoroughly investigated, no similar study has so far been devoted exclusively to 6-substituted nicotinic acids and some *para*-substituted benzoic acids.

#### RESULTS AND DISCUSSION

The mechanism of the reaction between a carboxylic acids and DDM has been thoroughly studied,<sup>5,10,17,18</sup> and found to involve the rate-determining proton transfer from the acid to DDM to form a diphenylmethanediazonium carboxylate ion-pair.<sup>10,11,14</sup>



The rate data for the reaction with DDM in twelve alcohols obtained in the present study as second order rate constants for the reactions of 6-substituted nicotinic acids, and for the *p*-CH<sub>3</sub> benzoic acid at 30 °C are given in Table I. The rate data for nicotinic acid, *p*-OH, and *p*-Cl benzoic acids are taken from our previous paper.<sup>3</sup>

TABLE I. Rate constants (dm<sup>3</sup> mol<sup>-1</sup> min<sup>-1</sup>) for the reaction of 6-substituted nicotinic acids and *p*-substituted benzoic acids with DDM at 30 °C in various alcoholic solvents

Solvent	H	4-Cl	4-OH	4-CH <sub>3</sub>	3N	6-Cl-3N	6-OH-3N	6-CH <sub>3</sub> -3N
Methanol	2.46 <sup>a</sup>	4.05 <sup>d</sup>	1.29 <sup>d</sup>	1.88	10.69	13.51	6.13	7.7
Ethanol	0.99 <sup>a</sup>	1.8 <sup>a</sup>	0.533 <sup>d</sup>	0.84	5.4 <sup>f</sup>	7.94	3.4	4.6
Propan-1-ol	1.07 <sup>a</sup>	1.74 <sup>d</sup>	0.522 <sup>d</sup>	0.905	6.15	7.8	3.1	4.5
Butan-1-ol	0.99 <sup>a</sup>	1.43 <sup>d</sup>	0.410 <sup>d</sup>	0.70	4.77	6.31	2.71	3.5
Propan-2-ol	0.69 <sup>a</sup>	1.36 <sup>d</sup>	0.377 <sup>d</sup>	0.562	4.40	6.03	2.4	3.2
Butan-2-ol	0.67 <sup>a</sup>	1.28 <sup>d</sup>	0.272 <sup>d</sup>	0.515	3.45	4.69	1.81	2.45
Cyclopentanol	0.74 <sup>c</sup>	1.45 <sup>d</sup>	0.333 <sup>d</sup>	0.602	3.67	4.97	1.96	2.8
2-Me-butan-2-ol	0.14 <sup>a</sup>	0.32 <sup>d</sup>	0.048 <sup>d</sup>	0.107	1.26	2.01	0.536	0.76
Pentan-1-ol	0.86 <sup>b</sup>	1.35 <sup>d</sup>	0.327 <sup>d</sup>	0.62	3.72	5.62	2.21	2.9
2-Me-propan-1-ol	1.67 <sup>a</sup>	2.35 <sup>d</sup>	0.695 <sup>d</sup>	1.21	6.97	9.28	3.76	4.9
2-Me-propan-2-ol	0.26 <sup>a</sup>	0.48 <sup>d</sup>	0.096 <sup>d</sup>	0.17	1.67	2.3	0.83	1.23
Benzyl alcohol	9.15 <sup>c</sup>	11.83 <sup>d</sup>	4.37 <sup>d</sup>	6.4	26.53	40.1	17.6	23.5

<sup>a</sup>Ref. 10, <sup>b</sup>Ref. 13, <sup>c</sup>Ref. 19, <sup>d</sup>Ref. 3, <sup>f</sup>Ref. 20

The results show (Table I) that the rate constants increase with increasing polarity of the solvent. This is in accordance with the proposed mechanism of the reaction.<sup>14,17,18</sup>

The  $\log k$  values of the investigated acids in all the alcoholic solvents used show a linear correlation with the corresponding literature values of  $\log k$  for the reaction of benzoic acid with DDM at 30 °C in the same solvents,<sup>10,13,19</sup> with correlation coefficients  $r$  and standard deviations  $s$  as given below. Nicotinic acid<sup>3</sup> ( $r = 0.9915$ ;  $s = 0.048$ ); 6-Cl-nicotinic acid ( $r = 0.9929$ ;  $s = 0.056$ ); 6-OH-nicotinic acid ( $r = 0.9931$ ;  $s = 0.055$ ); 6-CH<sub>3</sub>-nicotinic acid ( $r = 0.9947$ ;  $s = 0.049$ ); *p*-Cl-benzoic acid<sup>3</sup> ( $r = 0.9947$ ;  $s = 0.043$ ); *p*-OH-benzoic acid<sup>3</sup> ( $r = 0.9937$ ;  $s = 0.058$ ); *p*-CH<sub>3</sub>-benzoic acid ( $r = 0.9969$ ;  $s = 0.037$ ). Such linear free-energy intercorrelations indicate that the influence of the solvent properties is proportional in the series of substituted benzoic and heterocyclic acids in their reaction with DDM.

*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, a rate increase with increasing solvent polarity might be expected.<sup>21</sup>

Hence, we wanted to see if any correlation existed between the reaction rate and the relative permittivity  $\epsilon_r$ , or  $1/\epsilon_r$ , or the Kirkwood function<sup>22</sup> of the relative permittivity  $f(\epsilon) = (\epsilon_r - 1)/(2\epsilon_r + 1)$ . In all these cases, extremely poor correlations were obtained. The correlation of  $\log k$  with  $\sigma^*$ , the polar constant of the alkyl group<sup>23</sup> of the alcohol, was only satisfactory with  $r = 0.960$  for the 6-substituted nicotinic acids and  $r = 0.960$  for the *p*-substituted benzoic acids. Therefore, a multiple correlation of  $\log k$  with three solvent parameters,  $f(\epsilon)$ ,  $\sigma^*$  and  $n_{\gamma H}$ , as the works of Chapman *et al.*,<sup>12-16</sup> was used.

Chapman *et al.*<sup>15</sup> and other authors<sup>24</sup> have established that the solvent effect is best interpreted in terms of the following properties: (i) the behaviour of the solvent as a dielectric in facilitating the separation of opposite charges in the transition state; (ii) the ability of the medium to solvate the carboxylic acid molecule and thus stabilize the initial state relative to the transition state; and (iii) 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.

The Kirkwood function<sup>22</sup> of the relative permittivity  $\epsilon_r$ ,  $f(\epsilon) = (\epsilon_r - 1)/(2\epsilon_r + 1)$  is a suitable measure of the first property while the second and third property together are governed mainly by the polar effect of the alkyl group of the alcohol appropriately expressed by the Taft polar substituent constant  $\sigma^*$ .<sup>23</sup> Steric moderation of the second property also occurs, and this is suitably accounted for by  $n_{\gamma H}$ , the number of  $\gamma$ -hydrogen atoms in the alcohol.

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

TABLE II. Solvent parameters

Solvent	$\epsilon_r$	$f(\epsilon)$	$\sigma^*$	$n_{\gamma H}$
Methanol	32.70	0.477	0.000	0
Ethanol	24.55	0.470	-0.100	0
Propan-1-ol	20.33	0.464	-0.115	3
Butan-1-ol	17.51	0.457	-0.130	2
Propan-2-ol	19.41	0.460	-0.190	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
2-Me-propan-2-ol	12.47	0.434	-0.300	0
Benzyl alcohol	12.80	0.444	0.215	0

The multiple linear regression of  $\log k$  for the acids from Table I with  $f(\epsilon)$ ,  $\sigma^*$ , and  $n_{\gamma H}$  in the twelve alcoholic solvents are given by the following equations:

Nicotinic acid

$$\log k = (-0.424 \pm 0.367) + (3.019 \pm 0.793) f(\epsilon) + (2.259 \pm 0.144) \sigma^* + (0.022 \pm 0.009) n_{\gamma H} \quad (1)$$

with a multiple correlation coefficient  $r = 0.9897$  and a standard deviation of the estimate  $s = 0.058$

6-Cl-nicotinic acid

$$\log k = (-0.032 \pm 0.354) + (2.485 \pm 0.766) f(\epsilon) + (2.330 \pm 0.139) \sigma^* + (0.017 \pm 0.009) n_{\gamma H} \quad (2)$$

$(r = 0.9906; s = 0.056)$

6-OH-nicotinic acid

$$\log k = (-0.913 \pm 0.348) + (3.616 \pm 0.743) f(\epsilon) + (2.515 \pm 0.135) \sigma^* + (0.017 \pm 0.009) n_{\gamma H} \quad (3)$$

$(r = 0.9929; s = 0.054)$

6-CH<sub>3</sub>-nicotinic acid

$$\log k = (-0.882 \pm 0.258) + (3.766 \pm 0.558) f(\epsilon) + (2.491 \pm 0.101) \sigma^* + (0.019 \pm 0.007) n_{\gamma H} \quad (4)$$

$(r = 0.9960; s = 0.041)$

Benzoic acid

$$\log k = (-1.462 \pm 0.411) + (3.918 \pm 0.890) f(\epsilon) + (2.975 \pm 0.161) \sigma^* + (0.033 \pm 0.011) n_{\gamma H} \quad (5)$$

$(r = 0.9925; s = 0.065)$

*p*-Cl benzoic acid

$$\log k = (-1.054 \pm 0.420) + (3.467 \pm 0.908) f(\epsilon) + (2.580 \pm 0.165) \sigma^* + (0.018 \pm 0.011) n_{\gamma H} \quad (6)$$

$(r = 0.9898; s = 0.066)$

*p*-OH benzoic acid

$$\log k = (-2.584 \pm 0.434) + (5.685 \pm 0.938) f(\epsilon) + (3.075 \pm 0.170) \sigma^* + (0.023 \pm 0.011) n_{\gamma H} \quad (7)$$

( $r = 0.9930$ ;  $s = 0.068$ )

*p*-CH<sub>3</sub> benzoic acid

$$\log k = (-1.902 \pm 0.329) + (4.613 \pm 0.712) f(\epsilon) + (2.916 \pm 0.129) \sigma^* + (0.032 \pm 0.008) n_{\gamma H} \quad (8)$$

( $r = 0.9952$ ;  $s = 0.052$ )

The  $\log k$  values in Eqs. (2–4), and (8) are derived from the kinetic experiments performed in this work. The rate constants for nicotinic acid, *p*-Cl benzoic, *p*-OH-benzoic, and benzoic acids reacting with DDM in the same twelve alcoholic solvents, used in Eqs. (1), (5), (6), and (7), respectively, were taken from literature as specified in Table I.

After analyzing the above equations it can be said that the influence of relative permittivity, as a term of Kirkwood function, on the substituents at the *para* position in the benzoic acids is more important than on the substituents at the 6-position in the nicotinic acids. This is especially characteristic for electron donating substituents such as the OH group, which is confirmed by the differences of the Kirkwood function  $\Delta f(\epsilon)$  for electron donating substituent at the *para* position of benzoic acid and the 6-position of nicotinic acid. This is probably due to interactions of the solvent not only in the transition state but also with the substituent. The polarity of the solvent alkyl group, expressed by Taft polar constants  $\sigma^*$ , is considered to have the main influence on the rate of the chemical reactions in alcoholic solvents.<sup>25</sup> This was confirmed by the relatively good partial correlations with  $\sigma^*$  only, where the correlation coefficients were about  $r = 0.95$  and  $s = 0.15$  for all the investigated acids, in contrast to the individual correlations with the other solvent parameters,  $f(\epsilon)$  and  $n_{\gamma H}$ , which were poor.

The influence of  $\sigma^*$  is of almost the same intensity for substituents in position 6 of nicotinic acid and for *para* substituents in benzoic acid as the differences in coefficients associated with  $\sigma^*$  for substituents in position 6 of nicotinic acid and *para* substituents in benzoic acid are less than the corresponding differences in the coefficients associated with  $f(\epsilon)$ . The  $n_{\gamma H}$  term is generally needed to account for the observed rate enhancing effect of branching at the  $\beta$ -carbon atom of the alcohol.<sup>25</sup> In this work, the  $n_{\gamma H}$  term is statistically insignificant in all expressions.

*Variation of the Hammett reaction constant  $\rho$  with solvent in the reactions of the investigated acids with DDM*

The Hammett  $\rho$  values for the reaction of 6-substituted nicotinic acids and *p*-substituted benzoic acids in 12 alcohols were calculated using the values  $\sigma_p$ ,<sup>26</sup>  $\sigma_I$  and  $\sigma_R$ .<sup>27</sup> These values are given in Table III.

TABLE III. Values of Hammett  $\rho_p$ ,  $\rho_I$ , and  $\rho_R$  for the reaction of DDM with 6-substituted nicotinic acids and *para*-substituted benzoic acids in various alcohols at 30 °C

Solvent	6-substituted nicotinic acids 3N, 6-Cl-3N, 6-OH-3N, 6-CH <sub>3</sub> -3N			<i>para</i> -substituted benzoic acids H, 4-Cl, 4-OH, 4-CH <sub>3</sub>			$\rho_{1p}/\rho_{2p}$	$\rho_{1I}/\rho_{2I}$	$\rho_{1R}/\rho_{2R}$
	$\rho_{1p}$	$\rho_{1I}$	$\rho_{1R}$	$\rho_{2p}$	$\rho_{2I}$	$\rho_{2R}$			
	Methanol	0.592	0.590	0.589	0.825	0.859			
Ethanol	0.606	0.630	0.582	0.857	0.903	0.814	0.707	0.698	0.715
Propan-1-ol	0.681	0.617	0.712	0.868	0.876	0.851	0.785	0.704	0.837
Butan-1-ol	0.629	0.625	0.626	0.908	0.830	0.943	0.693	0.753	0.664
Propan-2-ol	0.680	0.673	0.677	0.911	1.003	0.841	0.746	0.671	0.805
Butan-2-ol	0.706	0.694	0.707	1.100	1.092	1.081	0.642	0.636	0.654
Cyclopentanol	0.680	0.647	0.690	1.037	1.057	1.007	0.656	0.612	0.685
2-Me-butan-2-ol	0.987	1.012	0.965	1.343	1.328	1.327	0.735	0.762	0.727
Pentan-1-ol	0.680	0.723	0.647	1.019	0.934	1.054	0.667	0.774	0.614
2-Me-propan-1-ol	0.677	0.671	0.675	0.883	0.789	0.927	0.767	0.850	0.728
2-Me-propan-2-ol	0.747	0.706	0.762	1.173	1.172	1.157	0.637	0.602	0.659
Benzyl alcohol	0.582	0.624	0.547	0.739	0.677	0.769	0.788	0.922	0.711

The calculated average value of the solvent effects on the ratio  $\rho_{1p}/\rho_{2p} = 0.71$  (Table III), shows that attenuation of electronic effects in the pyridine nucleus is more efficient than in benzene, which agrees with the literature.<sup>2</sup>

The higher values of the reaction constants for *para*-substituted benzoic acids than 6-substituted nicotinic acids in all the investigated solvents (Table III) show that the susceptibility to polar substituents effects is greater for the *para*-benzoic than for the 6-substituted nicotinic acid system.

Starting from the assumption of similarity in the transmitting cavities for the 6-substituted nicotinic acids and *para*-substituted benzoic acids, the differences in the transmission of substituent effects through the benzene ring and the pyridine ring were ascribed to differences in polarizability of the ring systems. The pyridine ring is less polarizable than the benzene ring.

For the majority of the studied solvents, the results given in Table III show that the  $\rho$  values decrease with increasing relative permittivity. This may be explained in ways that have been suggested by some authors before.<sup>28</sup> Evidently, at high relative permittivities, the energy necessary to bring about charge separation in the transition state is relatively small, which gives rise to a low susceptibility to the polar effects of the substituents. The  $\rho$  value, thus, increases as the energy necessary to achieve charge separation increases as  $\epsilon_r$  is decreased. Hence, it is reasonable to correlate  $\rho_1$  and  $\rho_2$  with the solvent parameters given in Table II, as it was done for  $\log k$ . From Table III for the 6-substituted nicotinic acids and for the *para*-substituted benzoic acids at 30 °C, the following relationships were obtained for the corresponding series of acids in twelve alcohols:

– for the 6-substituted nicotinic acids:

$$\rho_{1p} = (2.023 \pm 0.178) - (3.073 \pm 0.384) f(\epsilon) - (0.294 \pm 0.070) \sigma^* + (0.006 \pm 0.004) n_{\gamma H} \quad (9)$$

$$(r = 0.9744; s = 0.028, n = 12)$$

$$\rho_{1I} = (2.347 \pm 0.300) - (3.757 \pm 0.497) f(\epsilon) - (0.154 \pm 0.091) \sigma^* + (0.006 \pm 0.006) n_{\gamma H} \quad (10)$$

$$(r = 0.9602; s = 0.036, n = 12)$$

$$\rho_{1R} = (1.810 \pm 0.238) - (2.639 \pm 0.515) f(\epsilon) - (0.379 \pm 0.090) \sigma^* + (0.007 \pm 0.006) n_{\gamma H} \quad (11)$$

$$(r = 0.9553; s = 0.038, n = 12)$$

– for the *p*-substituted benzoic acids:

$$\rho_{2p} = (2.543 \pm 0.352) - (3.683 \pm 0.760) f(\epsilon) - (0.758 \pm 0.138) \sigma^* - (0.007 \pm 0.009) n_{\gamma H} \quad (12)$$

$$(r = 0.9604; s = 0.005, n = 12)$$

$$\rho_{2I} = (2.209 \pm 0.397) - (2.960 \pm 0.858) f(\epsilon) - (0.969 \pm 0.166) \sigma^* - (0.026 \pm 0.010) n_{\gamma H} \quad (13)$$

$$(r = 0.9551; s = 0.063, n = 12)$$

$$\rho_{2R} = (2.705 \pm 0.421) - (4.060 \pm 0.910) f(\epsilon) - (0.608 \pm 0.165) \sigma^* + (0.005 \pm 0.011) n_{\gamma H} \quad (14)$$

$$(r = 0.9420; s = 0.066, n = 12)$$

It should be noted that the dielectric term, compared with the  $\sigma^*$  term, contributes relatively more to the solvent dependence of  $\rho$  for the 6-substituted nicotinic acids but less for the *p*-substituted benzoic. This can be explained by the already mentioned fact that solvents with higher dielectric constants facilitate the separation of the opposite charges in the transition states relative to the initial state, which is more evident in the 6-substituted nicotinic acids because of the suppressed transmission effects through the pyridine ring system compared to the benzene ring system.

The contribution of the terms associated with  $n_{\gamma H}$  is small in all equations, but it probably accounts for the anomalously low values of  $\rho$  for 2-methyl-propan-1-ol considering to number of  $\gamma$ -hydrogens, just as the contribution of the  $n_{\gamma H}$  term in the equations serves mainly to account for the anomalously high value of the reaction constants in this alcohol. This has also been observed before.<sup>25</sup>

It is of interest to visualize how other solvent parameters, such as *Y* which refers to the ionization power of the solvent or the Dimroth-Reichert parameter  $E_T$ , correlate with the log rate constants.

The relationship of the log rate constants for the benzoic and nicotinic acids with the *Y* parameter yields fairly satisfactory correlation coefficients ( $r = 0.977$  and  $0.953$ , respectively) but cannot be discussed with confidence as the *Y* values for only four solvents were found in the literature.<sup>29</sup> On the other hand, the correlation of  $\log k$  and  $E_T$ <sup>30</sup> for the twelve solvents was not satisfactory ( $r = 0.784$  and  $0.630$ , respectively). It is evident that solvent effects on the studied reaction are more complex than can be explained by single parameter relationships.

However, the multiparameter relationships of  $\log k$  with  $E_T$  and the Lewis solvent basicity  $B$ <sup>30</sup> for the same two acids are:

$$\log k_{BA} = 16.46 - 0.032E_T - 0.124B$$

$$(n = 12, r = 0.955; s = 0.145)$$

for the benzoic acids and

$$\log k_{NA} = 12.53 - 0.019E_T - 0.091B$$

$$(n = 12, r = 0.958; s = 0.109)$$

for the nicotinic acids.

The same relationship for the reaction of benzoic acid with DDM in 23 alcoholic solvents at 37 °C found in the literature<sup>30</sup> is as follows:

$$\log k_{BA} = 15.94 - 0.03E_T - 0.118B$$

$$(n = 23, r = 0.9152; s = 0.167)$$

Evidently, there is good agreement of the values of the coefficients relating to  $E_T$  and  $B$  between our results and those cited in the literature.

The negative sign of the coefficient attached to  $B$  suggests nucleophilic stabilization of the carboxylic acid molecule by the solvent, indicating that the reaction rate decreases with increase solvent basicity. It is difficult to explain the negative sign of the  $E_T$  coefficients bearing in mind the reaction mechanism.<sup>10,11,14,18</sup> For aprotic solvents,<sup>30</sup> the sign of  $E_T$  is positive which indicates stabilization of the transition state by electrophilic solvation, as the  $E_T$  parameter includes the relative permittivity and Lewis acidity of the solvent.

On the basis of all the information presented, it may be concluded that linear free energy relationships are applicable to the kinetic data for 6-substituted nicotinic acids. The effects of alcoholic solvents on the rates of reaction of the investigated acids could be best interpreted by the parameters  $f(\epsilon)$ ,  $\sigma^*$ ,  $n_{\gamma H}$  used in the present paper. Solvent effects on  $\rho$  were also studied by multiple linear correlations with the same three solvent parameters which appeared to be a quite successful approach.

## EXPERIMENTAL

### Materials

Commercial samples of the acids were recrystallised. Their m.p.s. were identical or very close to those given in the literature.

Diazodiphenylmethane was prepared by the Smith and Howard method,<sup>31</sup> stock solution of ca. 0.06 mol dm<sup>-3</sup> was stored in a refrigerator and diluted immediately before use.

The solvents were purified as described in the literature.<sup>10</sup> Methanol was purified by the Lund and Bjerrum method<sup>32</sup> and ethanol by the Smith method.<sup>33</sup> Propan-1-ol, buta-1-ol, butan-2-ol and 2-methylpropan-1-ol were dried by methods analogous to the Smith method for ethanol. 2-Methylpropan-2-ol was dried over potassium carbonate, then refluxed over and distilled from sodium. 2-Methylbutan-2-ol was conveniently dried by fractional distillation, water being removed as an azeotrope of b.p. 88 °C. Cyclopentanol, pentan-1-ol, and benzyl alcohol were kept over freshly ignited potassium carbonate for some days and then treated with molecular sieve (Linde tipe 4Å) for at least 3 days. The solvents were then distilled under reduced pressure.



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

#### *Kinetic measurements*

The rate constants  $k$ , for the reaction of 6-substituted nicotinic acids and  $p$ -CH<sub>3</sub>-benzoic acid with DDM were determined as reported previously by the spectroscopic method of Roberts and coworkers<sup>4</sup> using a SHIMADZU 160A spectrophotometer. Optical density measurements were performed at 525 nm with 1 cm cells at 30±0.05 °C.

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

All regression analyses in this work were carried out with the ICL Statistical Analysis Package Mark 2×DS3. All the above correlations are significant between 99 % and 99.9 % confidence limits.

### ИЗВОД

#### КИНЕТИКА РЕАЦИЈА 6-СУПСТИТУИСАНИХ НИКОТИНСКИХ КИСЕЛИНА И НЕКИХ $p$ -СУПСТИТУИСАНИХ БЕНЗОЕВИХ КИСЕЛИНА СА ДИАЗОДИФЕНИЛМЕТАНОМ У РАЗЛИЧИТИМ АЛКОХОЛИМА

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Одређене су константе брзине реакције естерификације 6-супституисаних никотинских киселина са супституентима Н, Cl, OH и CH<sub>3</sub> као и константе брзине за 4-CH<sub>3</sub> бензоову киселину са DDM на 30 °C у дванаест алкохолних растварача, коришћењем познате UV-спектрофотометријске методе. На основу добијених константи брзина реакција никотинских киселина и  $p$ -супституисаних бензоєвих киселина, коришћењем Hammett-ове једначине одређене су реакционе константе  $\rho$  за обе серије једињења и дискутован је начин преношења ефеката супституената кроз пиридинов и бензолов прстен. Вишеструком регресионом анализом успостављена је задовољавајућа зависност константи брзина реакција као и реакционе константе  $\rho$  са параметрима растварача као што су: Kirkwood-ова функција релативне пермитивности  $f(\epsilon)$ , Тафтова  $\sigma^*$  константа за алкил групе алкохола и  $n_{DH}$  који представља број  $\gamma$ -водоникових атома у алкохолу.

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