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# A linear solvation energy relationship study for the reactivity of 2-substituted cyclohex-1-enecarboxylic and 2-substituted benzoic acids with diazodiphenylmethane in aprotic and protic solvents

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*Abstract*: The rate constants for the reaction of 2-substituted cyclohex-1-enecarboxylic acids and the corresponding 2-substituted benzoic acids with diazodiphenylmethane were determined in various aprotic solvents at 30 ºC. In order to explain the kinetic results through solvent effects, the second order rate constants of the reaction of the examined acids were correlated using the Kamlet–Taft solvatochromic equation. The correlations of the kinetic data were carried out by means of multiple linear regression analysis and the solvent effects on the reaction rates were analyzed in terms of the contributions of the initial and transition state. The signs of the equation coefficients support the proposed reaction mechanism. The quantitative relationship between the molecular structure and the chemical reactivity is discussed, as well as the effect of geometry on the reactivity of the examined molecules.

*Keywords*: carboxylic acids, linear solvation energy relationship, diazodiphenylmethane, aprotic solvents, protic solvents.

## INTRODUCTION

Related to the study of the influence of the solvent on the reactivity[1–3] of organic molecules, previous work is extended in this paper towards the reactivity of $\alpha,\beta$-unsaturated carboxylic acids in their reaction with diazodiphenylmethane (DDM) in various aprotic and protic solvents. In a previous study, the reactivity of 2-substituted cyclohex-1-enecarboxylic acids with DDM in various alcohols was investigated.[1] The rate data for these acids were correlated with the simple and extended Hammett equations. The results showed that linear free energy relationships (LFER) are applicable to the kinetic data for the 2-substituted cyclohex--1-enylcarboxylic acid system. In a recent paper,[2] hydroxylic solvent effects were examined on the reaction of $\alpha,\beta$-unsaturated carboxylic acids with DDM by means

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of the linear solvation energy relationship (LSER) concept, developed by Kamlet *et al.*[4] The correlation equations obtained by stepwise regression for all the examined acids showed that the most successful approach, which aids the hydroxylic solvent effects in the reaction to be understood, lies in the separate correlations of the kinetic data with the hydrogen bond donating (HBD) and the hydrogen bond accepting (HBA) ability of the solvent. Multiple linear regression analysis (MLRA) is very useful in separating and quantifying such interactions of the examined reactivity. The first comprehensive application of multiple linear regression analysis to kinetic phenomena was that of Koppel and Palm,[5] who listed regression constants for the simple Koppel–Palm equation, for various processes. Aslan *et al.*[6] showed that correlation analysis of second-order rate constants for the reaction of benzoic acid with DDM in hydroxylic solvents did not give satisfactory results with the Koppel–Palm model.[5] They came to the conclusion that the possibility of Koppel–Palm analysis of data related to protic solvents depends on the fitting of data in a regression with the main lines being determined by a much larger number of aprotic solvents. To the best of our knowledge, the influence of aprotic solvents on the reactivity of carboxylic acids with DDM by the Kamlet–Taft treatment has not been systematically presented before, except for benzoic acid.[7]

This paper demonstrates how the linear solvation energy relationship method can be used to explain and present multiple interacting effects of the solvent on the reactivity of 2-substituted cyclohex-1-enecarboxylic and 2-substituted benzoic acids in their reaction with DDM and the influence of the substituents of different nature at the C-2 position for the reactions in a given solvent set.

## RESULTS AND DISCUSSION

The second order rate constants for the reaction of various 2-substituted cyclohex-1-enecarboxylic acids and 2-substituted benzoic acids with DDM in eleven aprotic solvents at 30 °C were determined. In order to explain the kinetic results through solvent effects, the second order rate constants of the examined acids in aprotic solvents, together with the previously determined second-order rate constants for the same acids in hydroxylic solvents,[1,2] were correlated using the total solvatochromic equation, of the form:

$$\log k = A_0 + s\pi^* + a\alpha + b\beta \qquad (1)$$

where $\alpha$ and $\beta$ are solvatochromic parameters, $s$, $a$ and $b$ are solvatochromic coefficients, and $A_0$ is the regression value of the examined solute property in the reference solvent, cyclohexane.

In Eq. (1), $\pi^*$ 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 effect. The $\pi^*$ scale was selected to run from 0.00 for cyclohexanone to 1.00 for dimethyl sulphoxide.

The $\alpha$ parameter represents the scale of solvent hydrogen bond donor (HBD) acidity and has a range from 0.00 for non-HBD solvents (*e.g. n*-hexane, cyclohexane) to 1.00 for methanol. It describes the ability of a solvent to donate a proton, or accept an electron pair in a solvent-to-solute hydrogen bond. The $\beta$ parameter represents the scale of solvent hydrogen bond acceptor (HBA) basicity, in other words, the ability of a solvent to donate an electron pair, or accept a proton in a solvent-to-solute hydrogen bond. The $\beta$ scale runs from 0.00 for non-HBA solvents (*e.g. n*-hexane) to about 1.00 for hexamethylphosphoric acid triamide.

The obtained second-order rate constants for the examined cyclohex-1-enecarboxylic and benzoic acids in eleven aprotic solvents, together with the previously determined rate constants for the same acids in the hydroxylic solvents, are given in Tables I and II.

TABLE I. Reaction rate constants for the reaction of 2-substituted cyclohex-1-enecarboxylic acids with diazodiphenylmethane at 30 °C in various solvents

| Solvent | $k$ / dm$^3$ mol$^{-1}$min$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | Cyclohex--1-enecarboxylic acid | 2-Methylcyclohex-1-enecarboxylic acid | 2-Ethylcyclohex-1-enecarboxylic acid | 2-Chlorocyclohex-1-enecarboxylic acid | 2-Bromocyclohex-1-enecarboxylic acid | 2-Iodocyclohex-1-enecarboxylic acid |
| Methyl acetate | 0.032 | 0.093 | 0.095 | 0.563 | 0.614 | 0.642 |
| Cyclohexanone | 0.020 | 0.044 | 0.099 | 0.531 | 0.583 | 0.603 |
| Diethyl ketone | 0.053 | 0.064 | 0.110 | 0.583 | 0.634 | 0.653 |
| Carbon tetrachloride | 0.329 | 0.359 | 0.256 | 0.795 | 1.006 | 1.036 |
| Ethyl acetate | 0.025 | 0.058 | 0.082 | 0.501 | 0.574 | 0.606 |
| Cyclopentanone | 0.025 | 0.053 | 0.108 | 0.569 | 0.614 | 0.658 |
| Dioxane | 0.065 | 0.077 | 0.046 | 0.554 | 0.646 | 0.684 |
| Acetone | 0.048 | 0.106 | 0.116 | 0.680 | 0.831 | 0.891 |
| Methanol | 0.817 | 0.567 | 0.583 | 2.244 | 2.321 | 2.614 |
| Ethanol | 0.417 | 0.264 | 0.278 | 1.130 | 1.279 | 1.470 |
| Dimethyl sulfoxide | 0.008 | 0.013 | 0.060 | 0.198 | 0.210 | 0.230 |
| Tetrahydrofuran | 0.019 | 0.027 | 0.055 | 0.179 | 0.191 | 0.204 |
| Acetonitrile | 0.318 | 0.420 | 0.347 | 1.580 | 1.623 | 1.782 |
| Ethylene glycol | 1.962 | 1.631 | 1.649 | 5.222 | 5.169 | 5.738 |

The obtained results show that the rate constants increase with increasing solvent polarity. Comparison of the values of the reaction constants in protic and aprotic solvents indicates that the examined reaction is slower in aprotic solvents, which is in accordance with the proposed reaction mechanism.[8–11] The mechanism of this reaction in both protic and aprotic solvents was found to involve the same rate-determining step: proton transfer from the carboxylic acid to DDM,

forming a diphenylmethanediazonium carboxylate ion pair, which rapidly reacts to give esters, or ethers in the case of hydroxylic solvents:

$$Ph_2CN_2 + RCOOH \rightarrow Ph_2CHN_2^+O_2^-CR$$

TABLE II. Reaction rate constants for the reaction of 2-substituted benzoic acids with diazodiphenylmethane at 30 °C in various solvents

| Solvent | $k$ / dm$^3$ mol$^{-1}$ min$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | Benzoic acid | 2-Methyl-benzoic acid | 2-Ethylben-zoic acid | 2-Chloro-benzoic acid | 2-Bromoben-zoic acid | 2-Iodo-benzoic acid |
| Methyl acetate | 0.260 | 0.124 | 0.130 | 1.543 | 1.620 | 1.720 |
| Cyclohexanone | 0.220 | 0.129 | 0.138 | 1.393 | 1.510 | 1.580 |
| Diethyl ketone | 0.265 | 0.157 | 0.160 | 1.510 | 1.690 | 1.760 |
| Carbon tetrachloride | 0.638 | 0.389 | 0.496 | 1.200 | 1.380 | 1.412 |
| Ethyl acetate | 0.180 | 0.094 | 0.106 | 1.479 | 1.480 | 1.590 |
| Cyclopentanone | 0.293 | 0.145 | 0.154 | 1.530 | 1.620 | 1.780 |
| Dioxane | 0.058 | 0.035 | 0.048 | 0.750 | 0.758 | 0.813 |
| Acetone | 0.350 | 0.152 | 0.170 | 2.087 | 2.440 | 2.680 |
| Methanol | 2.470 | 1.860 | 2.526 | 12.71 | 13.75 | 15.22 |
| Ethanol | 0.995 | 0.933 | 0.986 | 4.388 | 5.627 | 5.960 |
| Dimethyl sulfoxide | 0.141 | 0.079 | 0.072 | 0.512 | 0.522 | 0.586 |
| Tetrahydrofuran | 0.105 | 0.060 | 0.062 | 0.454 | 0.464 | 0.482 |
| Acetonitrile | 3.730 | 1.590 | 1.654 | 5.852 | 6.023 | 6.759 |
| Ethylene glycol | 4.020 | 2.590 | 2.680 | 10.69 | 11.08 | 11.84 |

The previous investigations of the reactivity of $\alpha,\beta$-unsaturated carboxylic acids with DDM in various solvents[1–3] established that the characteristics of a solvent on the reaction rate should be given in terms of the following solvent properties: (*i*) the behaviour of a solvent as a dielectric, facilitating the separation of opposite charges in the transition state; (*ii*) the ability of a 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 a solvent to donate an electron pair and thereby stabilize the initial carboxylic acid, through a hydrogen bond between the carboxylic proton and the solvent electron pair. The parameter $\pi^*$ is an appropriate measure of the first property, while the second and the third properties are governed by the effects of the solvent acidity and basicity, expressed quantitatively by the parameters $\alpha$ and $\beta$, respectively.

*Solvent – reactivity relationship*

In order to explain the obtained kinetic results through solvent dipolarity/polarizability and basicity or acidity, the rate constants of the examined acids were correlated with the solvent properties using the total solvatochromic Equation (1). The solvent parameters[12] are given in Table III.

TABLE III. Solvent parameters

| Solvent | $\pi^*$ | $\alpha$ | $\beta$ |
|---|---|---|---|
| Methyl acetate | 0.60 | 0.00 | 0.42 |
| Cyclohexanone | 0.76 | 0.00 | 0.53 |
| Diethyl ketone | 0.72 | 0.00 | 0.45 |
| Carbon tetrachloride | 0.28 | 0.00 | 0.00 |
| Ethyl acetate | 0.55 | 0.00 | 0.45 |
| Cyclopentanone | 0.76 | 0.00 | 0.52 |
| Dioxane | 0.55 | 0.00 | 0.37 |
| Acetone | 0.72 | 0.08 | 0.48 |
| Methanol | 0.60 | 0.93 | 0.62 |
| Ethanol | 0.54 | 0.83 | 0.77 |
| Dimethyl sulfoxide | 1.00 | 0.00 | 0.76 |
| Tetrahydrofuran | 0.58 | 0.00 | 0.55 |
| Acetonitrile | 0.85 | 0.19 | 0.31 |
| Ethylene glycol | 0.92 | 0.90 | 0.52 |

The correlation of the kinetic data was performed by means of multiple linear regression analysis. It was found that the rate constants in the applied set of fourteen solvents show satisfactory correlation with the $\pi^*$,$\alpha$ and $\beta$ solvent parameters together in the same equation. The obtained correlation results are given in Table IV.

TABLE IV. The result of the correlation of the kinetic data with Eq. (1)

| Acid | $A_0$ | $s$[a] | $a$[a] | $b$[a] | $R$[b] | $sd$[c] | $F$[d] | $N$[e] |
|---|---|---|---|---|---|---|---|---|
| Cyclohex-1-enecarboxylic acid | –0.58 | 0.38±0.20 | 2.07±0.09 | –2.48±0.21 | 0.990 | 0.11 | 168 | 14 |
| 2-Methylcyclohex-1-ene-carboxylic acid | –0.49 | 0.52±0.16 | 1.66±0.07 | –2.35±0.17 | 0.989. | 0.09 | 162 | 14 |
| 2-Ethylcyclohex-1-ene-carboxylic acid | –0.93 | 0.87±0.21 | 1.24±0.10 | –1.51±0.22 | 0.972 | 0.12 | 58 | 14 |
| 2-Chlorocyclohex-1-ene-carboxylic acid | –0.18 | 0.75±0.21 | 1.07±0.10 | –1.42±0.22 | 0.960 | 0.12 | 39 | 14 |
| 2-Bromocyclohex-1-ene-carboxylic acid | –0.05 | 0.64±0.22 | 1.04±0.10 | –1.42±0.23 | 0.954 | 0.13 | 20 | 14 |
| 2-Iodocyclohex-1-ene-carboxylic acid | –0.05 | 0.65±0.22 | 1.07±0.10 | –1.40±0.23 | 0.957 | 0.13 | 36 | 14 |
| Benzoic acid | –0.64 | 1.34±0.47 | 1.51±0.22 | –1.98±0.49 | 0.915 | 0.26 | 17 | 14 |
| 2-Methylbenzoic acid | –0.83 | 1.05±0.44 | 1.64±0.20 | –1.75±0.46 | 0.932 | 0.25 | 22 | 14 |
| 2-Ethylbenzoic acid | –0.71 | 0.92±0.29 | 1.81±0.13 | –1.79±0.31 | 0.973 | 0.10 | 75 | 14 |
| 2-Chlorobenzoic acid | 0.15 | 0.93±0.19 | 1.28±0.09 | –1.33±0.20 | 0.978 | 0.10 | 75 | 14 |
| 2-Bromobenzoic acid | 0.29 | 0.83±0.19 | 1.28±0.09 | –1.25±0.20 | 0.976 | 0.11 | 70 | 14 |
| 2-Iodobenzoic acid | 0.20 | 0.89±0.19 | 1.31±0.09 | –1.27±0.21 | 0.977 | 0.11 | 71 | 14 |

[a]Calculated solvatochromic coefficient; [b]correlation coefficient; [c]standard deviation of the estimate; [d]Fisher's test; [e]number of the points used in the calculations

From the results presented in Table IV, the general conclusion can be reached that the solvent effects influence the carboxylic acid–DDM reaction by two opposite contributions. The opposite signs of the electrophilic and the nucleophilic parameters are, as expected, in accordance with the described mechanism of the reaction. The positive signs of the *s* and *a* coefficients prove that the classical solvation and HBD effects increase the reaction rate, supporting the formation of the transition state, and the negative sign of the *b* coefficient indicates that HBA effects decrease the reaction rate and stabilize the state before the reaction begins. From the values of regression coefficients, the contribution of each parameter to reactivity, on a percentage basis, was calculated and is listed in Table V.

TABLE V. The percentage contributions of Kamlet–Taft's solvatochromic parameters to the reactivity

| Acid | $\pi^*$ / % | $\alpha$ / % | $\beta$ / % |
|---|---|---|---|
| Cyclohex-1-enecarboxylic acid | 8 | 42 | 50 |
| 2-Methylcyclohex-1-enecarboxylic acid | 11 | 37 | 52 |
| 2-Ethylcyclohex-1-enecarboxylic acid | 24 | 34 | 42 |
| 2-Chlorocyclohex-1-enecarboxylic acid | 23 | 33 | 44 |
| 2-Bromocyclohex-1-enecarboxylic acid | 21 | 34 | 46 |
| 2-Iodocyclohex-1-enecarboxylic acid | 21 | 34 | 45 |
| Benzoic acid | 28 | 31 | 41 |
| 2-Methylbenzoic acid | 24 | 37 | 39 |
| 2-Ethylbenzoic acid | 20 | 40 | 40 |
| 2-Chlorobenzoic acid | 26 | 36 | 38 |
| 2-Bromobenzoic acid | 25 | 38 | 37 |
| 2-Iodobenzoic acid | 26 | 38 | 36 |

From these results, it can be noticed that the non-specific interactions ($\pi^*$) are less pronounced than the specific ones ($\alpha$,$\beta$) in both carboxylic acid systems. However, the specific interactions have more influence on the cyclohexenyl than on the benzoic system. This probably means that the carboxyl group of the cyclohexenyl acids is more susceptible to the proton-donor and proton-acceptor solvent effects than the carboxyl group of the benzoic acids.

In order to obtain a complete view of the solvent interactions with the molecules of the examined carboxylic acids, the solvent effects are expressed quantitatively for every acid and refer separately to the reactants and the transition state in Table VI.

Higher reaction rates and a more pronounced effect of the HBD solvation and non-specific interactions (polarity/polarizability) can be noticed for halogen-substituted acids in both systems. As the negative inductive effect of the halogen at C-2 stabilizes the carboxylic anion, it supports the transition state, thus accelerating the reaction.

TABLE VI. The solvent effects

| Acid | HBA solvation $\beta$ / % | Sum of HBD solvation ($\alpha$ / %) and non-specific interactions ($\pi^*$ / %) |
|---|---|---|
| Cyclohex-1-enecarboxylic acid | 50 | 50 |
| 2-Methylcyclohex-1-enecarboxylic acid | 52 | 48 |
| 2-Ethylcyclohex-1-enecarboxylic acid | 42 | 58 |
| 2-Chlorocyclohex-1-enecarboxylic acid | 44 | 56 |
| 2-Bromocyclohex-1-enecarboxylic acid | 46 | 54 |
| 2-Iodocyclohex-1-enecarboxylic acid | 45 | 55 |
| Benzoic acid | 41 | 59 |
| 2-Methylbenzoic acid | 39 | 61 |
| 2-Ethylbenzoic acid | 40 | 60 |
| 2-Chlorobenzoic acid | 38 | 62 |
| 2-Bromobenzoic acid | 37 | 63 |
| 2-Iodobenzoic acid | 36 | 64 |

The results presented here show that the proton-acceptor solvent effects are somewhat more pronounced in the ground state for cyclohex-1-enecarboxylic acid and its 2-substituted derivatives than for benzoic acids, supporting the fact that the reaction rates are higher for benzoic acids. For the benzoic acid type, the dominant solvent effects are the proton-donor and non-specific interactions, characteristic for the transition state. This fact is likely to be a consequence of the degree of conjugation of the carboxylic group of the benzoic acids with the ring, in other words, the charge distribution in the carboxylic group, because of conjugation, makes the anion more stable and therefore the reaction faster. However, the more general conclusion arising from these results is that substituents at the C-2 position in both types of carboxylic acid have a secondary influence on the reaction with DDM and do not seem to cause steric hindrance between the reactants and the solvent. The principal influences on the reaction rate are apparently the solvent properties and the general form of the carboxylic acid molecule.

*Structure – reactivity relationship*

Taking into account the results presented in this work, it can be concluded that the solvation differences of the examined acids in their reaction with DDM derive from the structural differences between the cyclohex-1-enecarboxylic and benzoic acids. Such a conclusion can be drawn from the minimal energy molecular conformations. The geometric layout of the benzoic and cyclohex-1-enecarboxylic acids corresponding to the energy minima in solution were obtained using semi-empirical MNDO-PM3 energy calculations, as reported previously[13] and are shown in Figs. 1 and 2.

In the molecule of benzoic acid, the carboxylic group is almost planar with the ring (Fig. 1), which is the cause of the conjugation of the carbonyl group of the carboxylic group and the benzene ring. In the case of cyclohex-1-enecarboxylic acid (Fig. 2), the carboxylic group is 142° twisted out of the plane of the double bond and is of the opposite orientation compared to benzoic acid. The double bond of cyclohex-1-enecarboxylic acid is much closer to the carboxylic group, which can have consequently an interaction between the carboxylic proton and the π-electrons of the double bond. This is hardly possible for benzoic acid because the position of its carboxylic group is quite different.

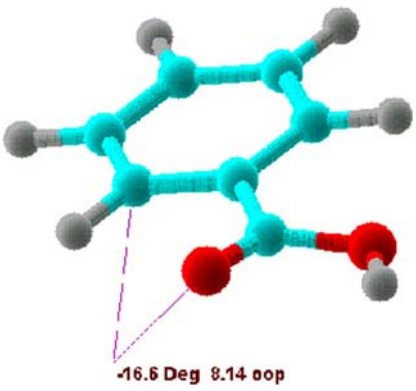


Fig. 1. The most stable conformation of benzoic acid.

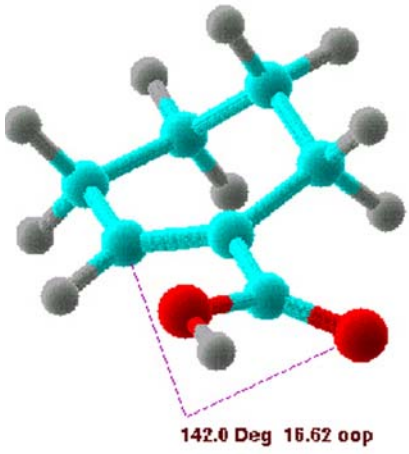


Fig. 2. The most stable conformation of cyclohex-1-enecarboxylic acid.

Additional evidence of the solvent effect on the structure–reactivity relationship in the reaction of 2-subsituted cyclohex-1-enecarboxylic and 2-subsitututed benzoic acids with DDM was also obtained by the correlation of the log *k* values for the examined acids with the Hammett Equation (2):[14]

$$\log k = \log k_0 + \rho\sigma_p \qquad (2)$$

where $\rho$ is the reaction constant, reflecting the sensitivity of log *k* to substituent effects. The substituent constant $\sigma_p$[15] is a measure of the electronic effects of a substituent. The results of the correlations are given in Tables VII and VIII.

The difference in the transmission of substituent effects through the benzene ring and the double bond in the cyclohexene ring were ascribed to the different polarizability of the double bonds of the examined compounds and the different solvent effects on the transmission of the substituent proximity effect at the C-2 position.

The poor correlation coefficients for the Hammett equations related to 2-substituted cyclohex-1-enecarboxylic acids, particularly in aprotic solvents, indicate that the cyclohex-1-enecarboxylic acid system is more sensitive to solvent effects

than the benzoic acid system, for which the Hammett equations have rather high, reliable correlation coefficients.

TABLE VII. Hammett reaction constants and correlation parameters for 2-substituted cyclohex-1-ene-carboxylic acids

| Solvent | $\rho$[a] | $r$[b] | $sd$[c] | $n$[d] |
|---|---|---|---|---|
| Methyl acetate | 2.38 | 0.799 | 0.37 | 6 |
| Cyclohexanone | 2.77 | 0.798 | 0.43 | 6 |
| Diethyl ketone | 2.49 | 0.883 | 0.27 | 6 |
| Carbon tetrachloride | 1.33 | 0.920 | 0.12 | 6 |
| Ethyl acetate | 2.66 | 0.820 | 0.38 | 6 |
| Cyclopentanone | 2.68 | 0.805 | 0.41 | 6 |
| Dioxane | 2.80 | 0.934 | 0.22 | 6 |
| Acetone | 2.48 | 0.834 | 0.34 | 6 |
| Methanol | 1.66 | 0.975 | 0.08 | 6 |
| Ethanol | 1.81 | 0.974 | 0.09 | 6 |
| Dimethyl sulfoxide | 2.64 | 0.756 | 0.47 | 6 |
| Tetrahydrofuran | 2.03 | 0.819 | 0.29 | 6 |
| Acetonitrile | 1.78 | 0.902 | 0.17 | 6 |
| Ethylene glycol | 1.40 | 0.964 | 0.08 | 6 |

[a]Reaction constant; [b]correlation coefficient; [c]standard deviation of the estimate; [d]number of the points used in the calculations

TABLE VIII. Hammett reaction constants and correlation parameters for 2-substituted benzoic acids

| Solvent | $\rho$[a] | $r$[b] | $sd$[c] | $n$[d] |
|---|---|---|---|---|
| Methyl acetate | 2.97 | 0.985 | 0.10 | 6 |
| Cyclohexanone | 2.84 | 0.977 | 0.13 | 6 |
| Diethyl ketone | 2.75 | 0.977 | 0.12 | 6 |
| Carbon tetrachloride | 1.28 | 0.977 | 0.06 | 6 |
| Ethyl acetate | 3.20 | 0.979 | 0.14 | 6 |
| Cyclopentanone | 2.79 | 0.983 | 0.10 | 6 |
| Dioxane | 3.50 | 0.964 | 0.20 | 6 |
| Acetone | 3.14 | 0.982 | 0.12 | 6 |
| Methanol | 2.22 | 0.949 | 0.15 | 6 |
| Ethanol | 2.04 | 0.936 | 0.16 | 6 |
| Dimethyl sulfoxide | 2.28 | 0.984 | 0.08 | 6 |
| Tetrahydrofuran | 2.38 | 0.973 | 0.09 | 6 |
| Acetonitrile | 1.50 | 0.973 | 0.07 | 6 |
| Ethylene glycol | 1.68 | 0.984 | 0.06 | 6 |

[a]Reaction constant; [b]correlation coefficient; [c]standard deviation of the estimate; [d]number of the points used in the calculations

Based on the results presented in this paper and previously reported results for more than fifty carboxylic acids, it can be concluded that the solvatochromic concept of Kamlet and Taft is applicable to the kinetic data for the reaction of different carboxylic acids with DDM in various solvents. This means that this model gives a correct interpretation of the solvating effects on the carboxylic group in various solvents. The solvation models for 2-substituted cyclohex-1-enecarboxylic and 2-substituted benzoic acids are suggested. The results show that the 2-substituted cyclohex-1-enecarboxylic acid system is more sensitive to aprotic solvent effects than the 2-substituted benzoic acid system.

## EXPERIMENTAL

Cyclohex-1-enecarboxylic, 2-methylcyclohex-1-enecarboxylic, 2-ethylcyclo-hex-1-enecarboxylic, 2-chlorocyclohex-1-enecarboxylic, 2-bromocyclohex-1-enecarboxylic and 2-iodo-cyclohex-1-enecarboxylic acids were prepared by the method of Wheeler and Lerner,[16] from the corresponding cyclohexanone cyanohydrine which was dehydrated to cyanocyclohexene. The nitrile was hydrolyzed with phosphoric acid to the corresponding cyclohex-1-enecarboxylic acid. Benzoic, 2-methylbenzoic, 2-ethylbenzoic, 2-chlorobenzoic, 2-bromobenzoic and 2-iodobenzoic acids were commercial products (Fluka, Germany).

The chemical structure and purity of the obtained compounds were confirmed by melting or boiling points, as well as $^1$H-NMR, FTIR and UV spectroscopy.

Diazodiphenylmethane was prepared by the method of Smith *et al.*[17] and stock solutions were stored in a refrigerator and diluted before use. Solvents were purified as described in previous papers.[8,18] All the solvents used in the kinetic studies were of analytical grade. Rate constants for the reaction of examined acids with DDM were determined as reported previously, by the spectroscopic method of Roberts and co-workers,[19] using a Shimadzu UV-1700 spectrophotometer. Optical density measurements were performed at 525 nm with 1 cm cells at 30±0.05 ºC. The second order rate constants for all acids were obtained by dividing the pseudo-first order rate constants by the acid concentration (the concentration of acid was 0.06 mol dm$^{-3}$ and of DDM 0.006 mol dm$^{-3}$). Three to five rate constant determinations were made for each acid in every case and, in particular, the second-order rate constants agreed within 3 % of the mean value. The correlation analyses were performed using Origin and Microsoft Excel computer software. The goodness of fit was discussed using the correlation coefficient (*R*), standard deviation (*s*) and the Fisher's value (*F*).

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## И З В О Д

## ПРОУЧАВАЊЕ РЕАКТИВНОСТИ 2-СУПСТИТУИСАНИХ ЦИКЛОХЕКС-1--ЕНКАРБОКСИЛНИХ И 2-СУПСТИТУИСАНИХ БЕНЗОЕВИХ КИСЕЛИНА У АПРОТИЧНИМ И ПРОТИЧНИМ РАСТВАРАЧИМА ПОМОЋУ ЛИНЕАРНЕ КОРЕЛАЦИЈЕ СОЛВАТАЦИОНИХ ЕНЕРГИЈА

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Константе брзине за реакцију 2-супституисаних циклохекс-1-енкарбоксилних и одговарајућих 2-супституисаних бензоевих киселина са диазодифенилметаном су одређене у низу

различитих апротичних растварача на температури од 30 °C. Да би се кинетички резултати објаснили помоћу ефеката растварача, добијене константе брзине реакције другог реда су корелисане Камлет–Тафтовом солватохромном једначином. Корелације кинетичких података су добијене помоћу методе вишеструке линеарне регресионе анализе и ефекти растварача су посебно анализирани у односу на основно и прелазно стање. Аритметички знаци испред коефицијената солватохромних параметара растварача одговарају претпостављеном механизму испитиване реакције. Такође је проучаван квантитативни однос молекулске структуре и реактивности, као и ефекат геометрије молекула испитиваних једињења на њихову реактивност.

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