

A Linear Solvation Energy Relationship Study for the Reactivity of 2-(4-Substituted Phenyl)-cyclohex-1-enecarboxylic, 2-(4-Substituted Phenyl)-benzoic, and 2-(4-Substituted Phenyl)-acrylic Acids with Diazodiphenylmethane in Various Solvents

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ABSTRACT: The reactivities of 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids, 2-(4-substituted phenyl)-benzoic acids, and 2-(4-substituted phenyl)-acrylic acids with diazodiphenylmethane in various solvents were investigated. To explain the kinetic results through solvent effects, the second-order rate constants 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 initial and transition state contributions. The signs of the equation coefficients support the proposed reaction mechanism. The solvation models for all investigated carboxylic acids are suggested. 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. © 2010 Wiley Periodicals, Inc. *Int J Chem Kinet* 42: 430–439, 2010

INTRODUCTION

Related to the study of the influence of the solvent on the reactivity [1–6] of organic molecules, previous work is extended toward the reactivity of α,β -unsaturated carboxylic acids in their reaction with diazodiphenylmethane (DDM) in various protic and aprotic solvents.

Kamlet et al. [7] established that the effect of a solvent on the reaction rate should be given in terms of the following properties: (i) the behavior 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 therefore stabilize the initial carboxylic acid, by way of a hydrogen bond between the carboxylic proton and the solvent electron pair, and used Eq. (1) to explain these properties:

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

The parameter π^* is an appropriate measure of the first property, whereas the second and the third properties are governed by the effects of the solvent acidity and basicity, quantitatively expressed by the parameters α and β , respectively. The linear dependence (LSER) on the solvent parameters is used to correlate and predict a wide variety of solvent effects, as well as to provide an analysis in the terms of knowledge and the theoretical concepts of the molecular structural effects [7].

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].

In recent papers [5,6,8,9], we examined the effects of a set of 11 aprotic and 3 protic solvents on the reaction of various carboxylic acids with DDM by means of the linear solvation energy relationship (LSER) con-

cept developed by Kamlet and Taft [7] (Eq. (1)). The correlation equations obtained by a stepwise regression for all the examined acids showed that the total solvatochromic equation can be used in its complete form.

The present paper demonstrates how the linear solvation energy relationship method can be used to explain and present multiple interacting effects of the solvents on the reactivity of 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids, 2-(4-substituted phenyl)-benzoic acids, and 2-(4-substituted phenyl)-acrylic acids (Fig. 1) in their reaction with DDM and the quantitative estimation of the solvent effects on the structure–reactivity relationship. The geometric data of the examined acids, corresponding to the energy minima in the applied solvents, were obtained using the semiempirical MO PM6 method.

MATERIALS AND METHODS

2-(4-Substituted phenyl)-cyclohex-1-enecarboxylic acids were prepared by the procedure for 2-substituted-cyclohex-1-enecarboxylic acids [10] from the corresponding 2-(4-substituted phenyl)-cyclohexanone by the cyanohydrine reaction as reported previously [11].

2-(4-Substituted phenyl)-benzoic acids were prepared from the corresponding 4-substituted aniline according to methods described in the literature [12].

2-(4-Substituted phenyl)-acrylic acids were prepared by saponification of the *cis*-ethyl cinnamates, synthesized by the hydrogenation of the appropriate ethyl-phenylpropionate over the Lindlar catalyst [13] as described previously [14].

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

Diazodiphenylmethane was prepared by the method described by Smith and Howard [15], and stock solutions were stored in a refrigerator and diluted

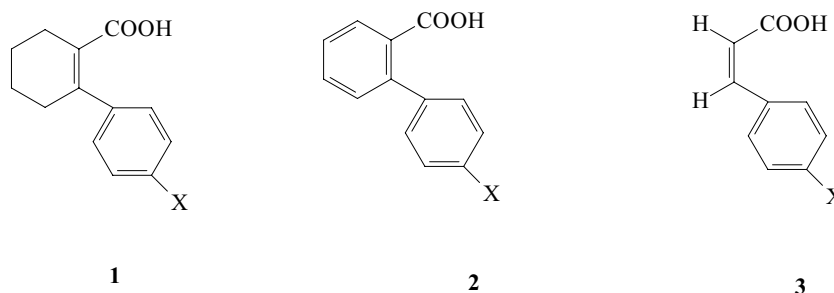


Figure 1 The structure of the investigated 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids (1), 2-(4-substituted phenyl)-benzoic acids (2), and 2-(4-substituted phenyl)-acrylic acids (3) ($X = \text{H}, \text{OCH}_3, \text{CH}_3, \text{Cl}, \text{Br}$).

before use. Solvents were purified as described in previous papers [16,17]. All the solvents used in kinetic studies were analytical grade. Rate constants for the reaction of examined acids with DDM were determined as reported previously, by the spectroscopic method of Roberts and his co-workers [18], using a Shimadzu UV-1700 spectrophotometer. Absorbance measurements were performed at 525 nm with 1-cm cells at $30 \pm 0.05^\circ\text{C}$. 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 $0.006 \text{ mol dm}^{-3}$). Three to five rate determinations were made on each acid in every case, and in particular the second-order rate constants agreed within 3% of the mean values. The correlation analysis was performed using Origin and Microsoft Excel computer software. The goodness of fit was discussed using correlation coefficient (R), standard deviation (SD), and the Fisher's value (F).

The reported conformations and the corresponding heats of formation of the examined molecules were obtained by the semiempirical MO PM6 method, using MOPAC 2007 program package [19]. The following keywords were used for optimization: EF GNORM = 0.100 MMOK GEO-OK PM6 EPS = xx PRECISE, where xx stands for the appropriate dielectric constant of a solvent (ethanol in this case).

RESULTS AND DISCUSSION

The second-order rate constants for the reaction of 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids, 2-(4-substituted phenyl)-benzoic acids, and 2-(4-substituted phenyl)-acrylic acids with DDM in 11 aprotic solvents at 30°C were determined. 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 [3,4] were correlated using the total solvatochromic equation (1), where π^* , α , and β are solvatochromic parameters; s , a , and b are the solvatochromic coefficients; and A_o is the regression value of the examined solute property in the reference solvent, cyclohexane.

In Eq. (1), π^* is an index of 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 π^* scale was selected to run from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide.

The α 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 β 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 β 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 acids in 11 aprotic solvents, together with the previously determined rate constants for the same acids in the hydroxylic solvents, are given in Tables I–III. Comparison of the values of the reaction constants in protic and aprotic solvents indicates that the examined reaction is slower in aprotic than in protic solvents, which is in agreement with the supposed reaction mechanism [20–22].

Solvent–Reactivity Relationship

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

Table I Second-Order Rate Constants ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$) for the Reaction of 2-(4-Substituted Phenyl)-cyclohex-1-enecarboxylic Acids with Diazodiphenylmethane at 30°C in a Set of Various Solvents

Solvent	k ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)				
	H	CH_3	OCH_3	Cl	Br
1. Methyl acetate	0.0681	0.0522	0.0442	0.0981	0.0982
2. Cyclohexanone	0.0382	0.0281	0.0242	0.0561	0.0563
3. Diethyl ketone	0.133	0.100	0.0851	0.194	0.195
4. Carbon tetrachloride	0.873	0.735	0.665	1.10	1.11
5. Ethyl acetate	0.0542	0.0411	0.0351	0.0782	0.078
6. Cyclopentanone	0.0491	0.0373	0.0322	0.0712	0.072
7. Dioxane	0.142	0.104	0.0873	0.216	0.217
8. Acetonitrile	0.839	0.703	0.635	1.06	1.07
9. Acetone	0.103	0.0811	0.0711	0.141	0.142
10. Methanol	2.79	2.32	2.032	3.44	3.81
11. Ethanol	1.28	1.07	0.924	1.71	1.87
12. Ethylene glycol	6.37	5.39	4.89	7.97	7.99
13. Dimethyl sulfoxide	0.0141	0.0113	0.00911	0.0191	0.0192
14. Tetrahydrofuran	0.0371	0.0272	0.0232	0.0551	0.0552

Table II Second-Order Rate Constants ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$) for the Reaction of 2-(4-Substituted Phenyl)-benzoic Acids with Diazodiphenylmethane at 30°C in a Set of Various Solvents

Solvent	k ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)				
	H	CH_3	OCH_3	Cl	Br
1. Methyl acetate	0.316	0.269	0.245	0.394	0.395
2. Cyclohexanone	0.246	0.207	0.188	0.310	0.311
3. Diethyl ketone	0.268	0.226	0.206	0.336	0.337
4. Carbon tetrachloride	1.01	0.909	0.856	1.163	1.16
5. Ethyl acetate	0.236	0.200	0.183	0.295	0.295
6. Cyclopentanone	0.338	0.285	0.259	0.425	0.426
7. Dioxane	0.110	0.091	0.0822	0.149	0.142
8. Acetonitrile	5.50	4.95	4.65	6.346	6.36
9. Acetone	0.400	0.348	0.322	0.482	0.483
10. Methanol	11.6	10.7	9.56	13.5	13.9
11. Ethanol	5.00	4.26	3.99	5.870	6.12
12. Ethylene glycol	15.4	13.9	13.1	17.6	17.6
13. Dimethyl sulfoxide	0.162	0.139	0.127	0.200	0.200
14. Tetrahydrofuran	0.147	0.123	0.111	0.186	0.187

equation (1). The solvent parameters [23] are given in Table IV. The correlation of the kinetic data was carried out by means of the multiple linear regression analysis. It was found that the rate constants in the applied set of 14 solvents show satisfactory correlation with π^* , α , and β solvent parameters together in the same equation. The obtained correlation results are given in Table V.

From the results presented in Table V, the general conclusion can be made 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 points out that HBA effects decrease the reaction rate and stabilize the state before the reaction begins. The degree of success of the above correlations is shown in Fig. 2 by means of a plot of $\log k$ calculated vs. $\log k$ obtained experimentally for 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic, 2-(4-substituted phenyl)-benzoic, and 2-(4-substituted phenyl)-acrylic acids in different solvents. From the values of regression coefficients, the contribution of each parameter to reactivity, on a percentage basis, was calculated and is listed in Table VI.

The percentage contribution of solvatochromic parameters, for the reaction of examined acids with

Table III Second-Order Rate Constants ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$) for the Reaction of 2-(4-Substituted Phenyl)-acrylic Acids with Diazodiphenylmethane at 30°C in a Set of Various Solvents

Solvent	k ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)				
	H	CH_3	OCH_3	Cl	Br
1. Methyl acetate	0.244	0.178	0.149	0.372	0.374
2. Cyclohexanone	0.151	0.108	0.089	0.236	0.237
3. Diethyl ketone	0.424	0.307	0.255	0.656	0.659
4. Carbon tetrachloride	2.00	1.64	1.46	2.63	2.64
5. Ethyl acetate	0.201	0.146	0.122	0.309	0.311
6. Cyclopentanone	0.186	0.134	0.111	0.289	0.290
7. Dioxane	0.447	0.312	0.253	0.727	0.732
8. Acetonitrile	1.94	1.58	1.40	2.56	2.57
9. Acetone	0.343	0.263	0.226	0.491	0.493
10. Methanol	5.28	4.62	3.86	7.44	7.87
11. Ethanol	2.58	2.26	1.83	3.76	4.11
12. Ethylene glycol	10.3	8.52	7.63	13.4	13.4
13. Dimethyl sulfoxide	0.0662	0.0491	0.0412	0.0991	0.0993
14. Tetrahydrofuran	0.147	0.105	0.086	0.232	0.233

DDM, show that the most of the solvatochromism is due to solvent basicity and acidity rather than to the solvent dipolarity/polarizability. Considering these results, the solvation models of the reactants and the transition states, separately for 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids, 2-(4-substituted phenyl)-benzoic acids, and 2-(4-substituted phenyl)-acrylic acids can be represented as

Generally, the presence of a substituent at the C-4 position on the benzene ring in all types of examined acids has 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.

2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids:

Reactants $\Rightarrow$ Transition state $\Rightarrow$ Products
 HBA solvation (51%) HBD and solvation by nonspecific interactions (49%)

2-(4-substituted phenyl)-benzoic acids:

Reactants $\Rightarrow$ Transition state $\Rightarrow$ Products
 HBA solvation (38%) HBD and solvation by nonspecific interactions (62%)

2-(4-substituted phenyl)-acrylic acids:

Reactants $\Rightarrow$ Transition state $\Rightarrow$ Products
 HBA solvation (50%) HBD and solvation by nonspecific interactions (50%)

The suggested solvation models indicate that the 2-phenylcyclohex-1-enecarboxylic and the 2-phenylacrylic acid systems are more sensitive to the HBA solvent interactions than the 2-phenylbenzoic acid system (Table VI) and less sensitive to the HBD solvent ability. The same results were obtained for a comparative LSER study of the reactivity of 2-substituted cyclohex-1-enecarboxylic and 2-substituted benzoic acids [8] and 2-substituted cyclohex-1-enecarboxylic and 2-substituted phenylacetic acids [9] presented in previous papers.

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-enylcarboxylic, benzoic, and the open-chain acrylic acids. Such a conclusion can be drawn from the minimal energy molecular conformations. The geometric layouts of the unsubstituted representatives of all carboxylic acid systems examined in this work,

Table IV Solvent Parameters [23]

Solvent	π^*	α	β
1. Methyl acetate	0.60	0.00	0.42
2. Cyclohexanone	0.76	0.00	0.53
3. Diethyl ketone	0.72	0.00	0.45
4. Carbon tetrachloride	0.28	0.00	0.00
5. Ethyl acetate	0.55	0.00	0.45
6. Cyclopentanone	0.76	0.00	0.52
7. Dioxane	0.55	0.00	0.37
8. Acetonitrile	0.85	0.19	0.31
9. Acetone	0.72	0.08	0.48
10. Methanol	0.60	0.93	0.62
11. Ethanol	0.54	0.83	0.77
12. Ethylene glycol	0.92	0.90	0.52
13. Dimethyl sulfoxide	1.00	0.00	0.76
14. Tetrahydrofuran	0.58	0.00	0.55

corresponding to the energy minima in solvent, were obtained using the semiempirical MO PM6 method and are shown in Figs. 3–5.

These geometrical conformations are taken into consideration because they are the most stable forms in which the examined molecules generally exist and

Table VI Percentage Contributions of Kamlet–Taft's Solvatochromic Parameters to the Reactivity

Acids	P_π^* (%)	P_α (%)	P_β (%)
2-Phenylcyclohex-1-enecarboxylic acid	6.50	43.50	50.00
2-(4-Methylphenyl)-cyclohex-1-enecarboxylic acid	7.00	47.50	45.50
2-(4-Methoxyphenyl)-cyclohex-1-enecarboxylic acid	6.70	42.90	50.40
2-(4-Chlorophenyl)-cyclohex-1-enecarboxylic acid	6.00	43.60	50.40
2-(4-Bromophenyl)-cyclohex-1-enecarboxylic acid	5.00	44.60	50.40
2-Phenylbenzoic acid	20.00	42.00	38.00
2-(4-Methylphenyl)-benzoic acid	20.00	42.00	38.00
2-(4-Methoxyphenyl)-benzoic acid	20.00	42.00	38.00
2-(4-Chlorophenyl)-benzoic acid	20.00	42.00	38.00
2-(4-Bromophenyl)-benzoic acid	20.00	42.00	38.00
2-Phenylacrylic acid	6.50	43.50	50.00
2-(4-Methylphenyl)-acrylic acid	6.00	44.00	50.00
2-(4-Methoxyphenyl)-acrylic acid	7.50	42.50	50.00
2-(4-Chlorophenyl)-acrylic acid	6.00	43.00	51.00
2-(4-Bromophenyl)-acrylic acid	5.00	45.00	50.00

Table V Results of the Correlations of the Kinetic Data with Eq. (1)

Acid	A_o	s^a	a^a	b^a	R^b	s^c	F^d	e^e
2-Phenylcyclohex-1-enecarboxylic acid	-0.140	0.35 ± 0.22	2.34 ± 0.10	-2.70 ± 0.24	0.991	0.13	175	14
2-(4-Methylphenyl)-cyclohex-1-enecarboxylic acid	-0.230	0.38 ± 0.24	2.39 ± 0.11	-2.30 ± 0.21	0.989	0.14	152	14
2-(4-Methoxyphenyl)-cyclohex-1-enecarboxylic acid	-0.290	0.38 ± 0.24	2.41 ± 0.11	-2.83 ± 0.26	0.988	0.14	136	14
2-(4-Chlorophenyl)-cyclohex-1-enecarboxylic acid	-0.002	0.32 ± 0.24	2.25 ± 0.11	-2.59 ± 0.26	0.988	0.14	136	14
2-(4-Bromophenyl)-cyclohex-1-enecarboxylic acid	0.010	0.27 ± 0.24	2.27 ± 0.11	-2.55 ± 0.26	0.988	0.14	138	14
2-Phenylbenzoic acid	-0.340	0.99 ± 0.41	2.11 ± 0.19	-1.90 ± 0.44	0.961	0.24	40	14
2-(4-Methylphenyl)-benzoic acid	-0.400	1.02 ± 0.42	2.15 ± 0.19	-1.96 ± 0.45	0.960	0.24	40	14
2-(4-Methoxyphenyl)-benzoic acid	-0.440	1.04 ± 0.43	2.17 ± 0.20	-1.99 ± 0.45	0.960	0.23	40	14
2-(4-Chlorophenyl)-benzoic acid	-0.260	0.97 ± 0.40	2.07 ± 0.19	-1.84 ± 0.42	0.962	0.23	41	14
2-(4-Bromophenyl)-benzoic acid	-0.260	0.95 ± 0.40	2.08 ± 0.19	-1.82 ± 0.43	0.961	0.23	41	14
2-Phenylacrylic acid	0.230	0.31 ± 0.19	1.92 ± 0.09	-2.25 ± 0.20	0.990	0.11	163	14
2-(4-Methylphenyl)-acrylic acid	0.130	0.30 ± 0.19	2.01 ± 0.09	-2.30 ± 0.21	0.989	0.11	160	14
2-(4-Methoxyphenyl)-acrylic acid	0.060	0.36 ± 0.19	2.03 ± 0.09	-2.38 ± 0.21	0.990	0.11	167	14
2-(4-Chlorophenyl)-acrylic acid	0.400	0.32 ± 0.24	2.25 ± 0.11	-2.59 ± 0.26	0.989	0.11	145	14
2-(4-Bromophenyl)-acrylic acid	0.410	0.21 ± 0.19	1.86 ± 0.09	-2.07 ± 0.21	0.988	0.11	139	14

^a Calculated solvatochromic coefficient.

^b Correlation coefficient.

^c Standard deviation of the estimate.

^d Fisher's test.

^e Number of points used in the calculation.

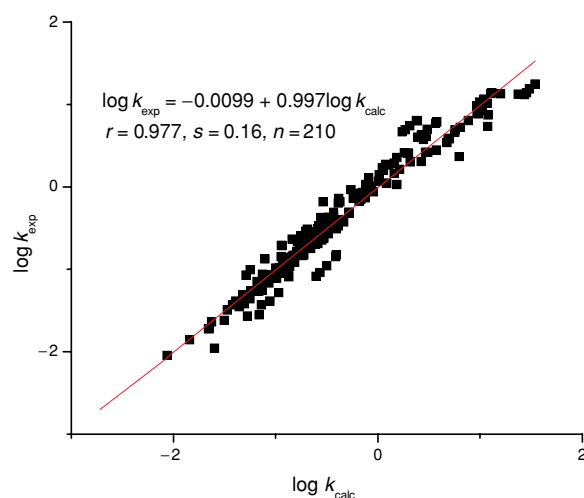


Figure 2 The plot of $\log k$ observed against $\log k$ calculated from Eq. (1) for 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic, 2-(4-substituted phenyl)-benzoic, and 2-(4-substituted phenyl)-acrylic acids in different solvents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

react; their torsion ($C_2-C_1-C_7-O_8$ or $C_2-C_1-C_3-O_4$) and the heats of formation corresponding to them are given in Table VII. Generally, the presence of the substituted phenylene group in the position 2 affects the orientation of the carboxylic group (torsion angles). The interactions of this type are the strongest in the case of 2-phenylbenzoic acid, weaker in the case of 2-phenylcyclohex-1-enecarboxylic acids, and in the case of 2-phenylacrylic acids they should not even be ex-

Table VII Data Calculated Using the Semiempirical MO PM6 Method

Acid	Torsion Angle (°)	Heat of Formation (kcal mol ⁻¹)
2-Phenylcyclohex-1-enecarboxylic acid	($C_2-C_1-C_7-O_8$) 134.8	-79.93
2-Phenylbenzoic acid	($C_2-C_1-C_7-O_8$) 132.5	-47.20
2-Phenylacrylic acid	($C_2-C_1-C_3-O_4$) 136.9	-57.14

pected (Figs. 3–5). The degree of these interactions is in agreement with the obtained kinetic data and solvation models for all the examined acids.

Additional evidence of the solvent effect on the structure–reactivity relationship in the reaction of the examined 2-phenyl-substituted carboxylic acids with DDM was also obtained by the correlation of $\log k$ values for the examined acids with the Hammett equation (2) [24]:

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

where ρ is the reaction constant, reflecting the sensitivity of $\log k$ to substituent effects. The substituent constant σ_p [25] is a measure of the electronic effects of a substituent. The results of the correlations are given in Tables VIII–X.

On the basis of the values of the reaction constants, it can be concluded that the resonance interactions are the least disturbed in the case of 2-(4-substituted phenyl)-acrylic acids, somewhat more in the case

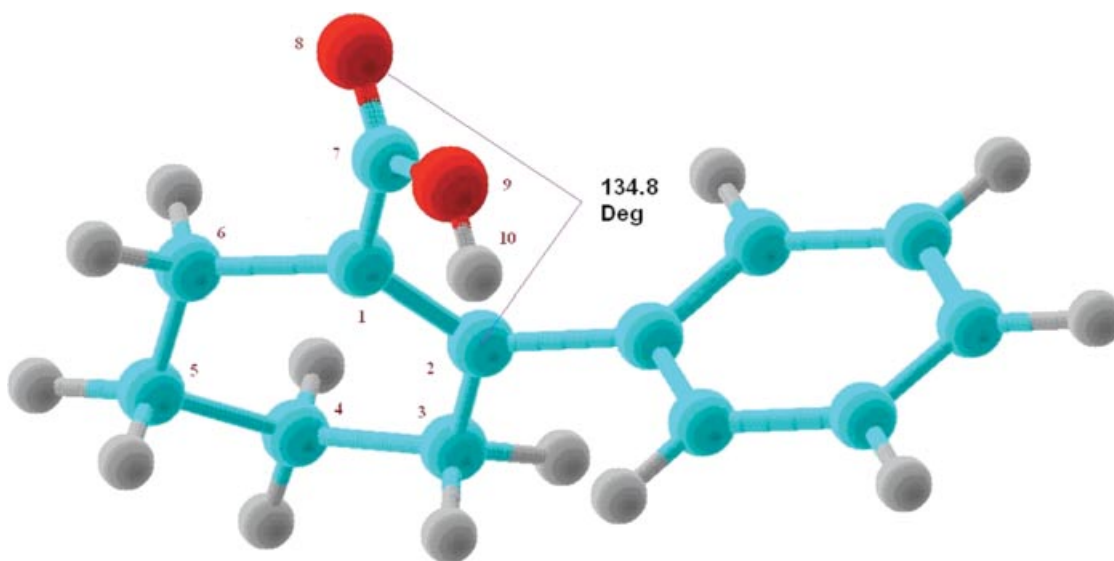


Figure 3 The most stable conformation of 2-phenylcyclohex-1-enecarboxylic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

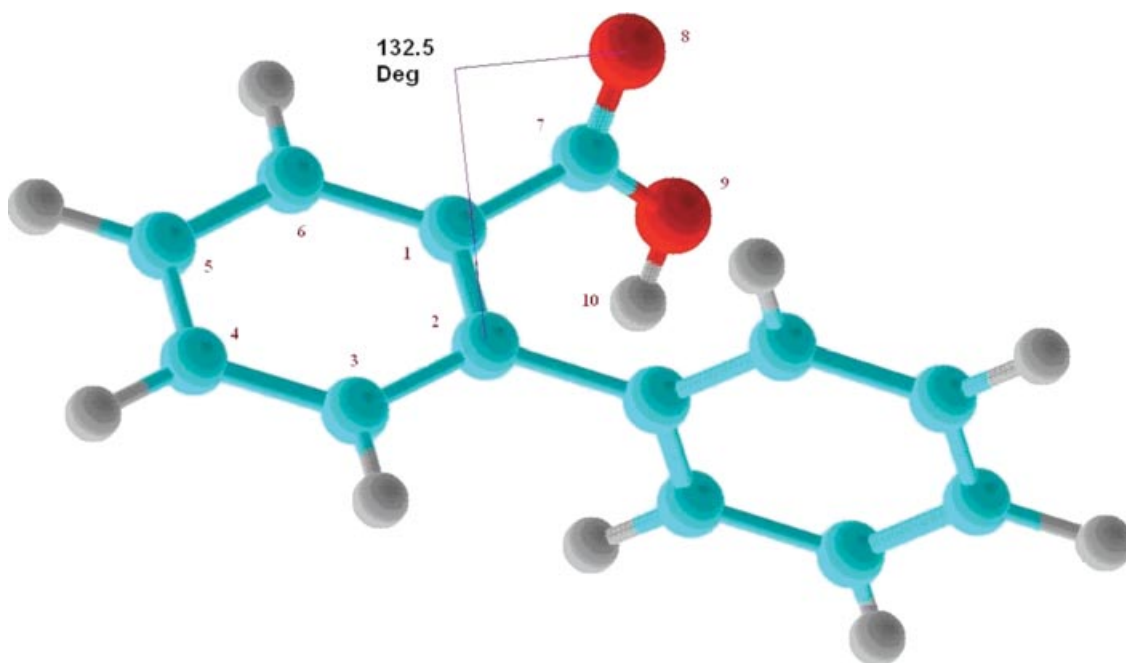


Figure 4 The most stable conformation of 2-phenylbenzoic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

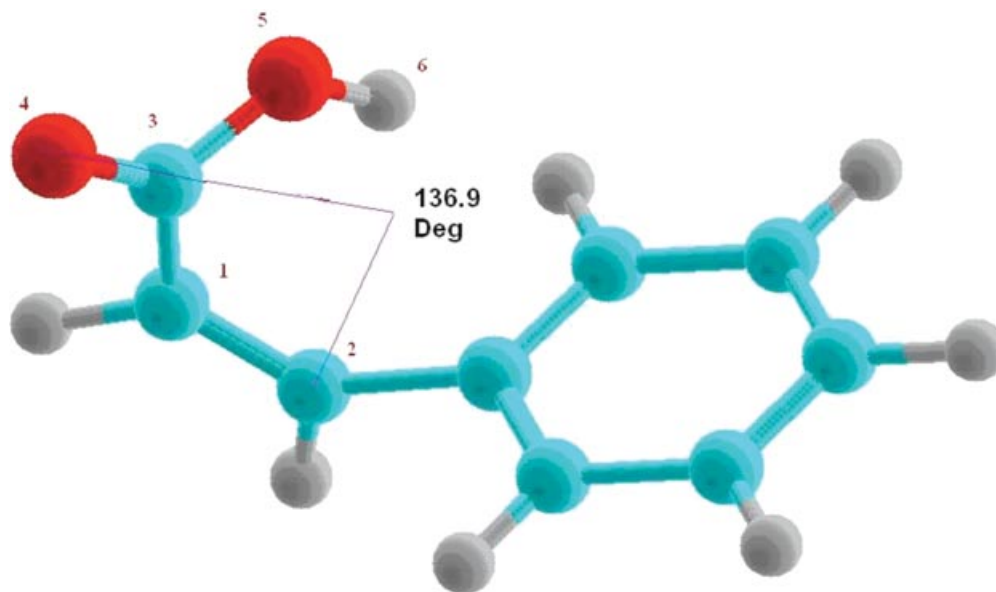


Figure 5 The most stable conformation of 2-phenylacrylic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids, and the most in the case of 2-(4-substituted phenyl)-benzoic acids.

These results are in agreement with the structural characteristics of the examined carboxylic acids obtained by the semiempirical MO PM6 method and the solvation models determined by the LSER method.

CONCLUSION

The results of the presented investigations and the previously reported results [5,6,8,9] show that the solvatochromic concept of Kamlet and Taft (LSER) is applicable to the kinetic data for the reaction of more than 50 different carboxylic acids with diazodiphenylmethane in various solvents, meaning that this model gives the

Table VIII Hammett Reaction Constants for 2-(4-Substituted Phenyl)-cyclohex-1-enecarboxylic Acids

Solvent	ρ^a	r^b	s^c	d^d
1. Methyl acetate	0.695 ± 0.004	0.999	0.0020	5
2. Cyclohexanone	0.745 ± 0.006	0.999	0.0030	5
3. Diethyl ketone	0.722 ± 0.002	0.999	0.0010	5
4. Carbon tetrachloride	0.441 ± 0.001	0.999	0.0005	5
5. Ethyl acetate	0.699 ± 0.001	0.999	0.0005	5
6. Cyclopentanone	0.706 ± 0.008	0.999	0.0030	5
7. Dioxane	0.795 ± 0.002	0.999	0.0008	5
8. Acetonitrile	0.452 ± 0.001	0.999	0.0050	5
9. Acetone	0.603 ± 0.003	0.999	0.0010	5
10. Methanol	0.498 ± 0.040	0.990	0.0180	5
11. Ethanol	0.571 ± 0.040	0.992	0.0180	5
12. Ethylene glycol	0.426 ± 0.001	0.999	0.0004	5
13. Dimethyl sulfoxide	0.632 ± 0.030	0.997	0.0120	5
14. Tetrahydrofuran	0.764 ± 0.006	0.999	0.0030	5

^a Reaction constant.^b Correlation coefficient.^c Standard deviation of the estimate.^d Number of points used in the calculation.**Table IX** Hammett Reaction Constants for 2-(4-Substituted Phenyl)-benzoic Acids

Solvent	ρ^a	r^b	s^c	d^d
1. Methyl acetate	0.415 ± 0.001	0.999	0.0006	5
2. Cyclohexanone	0.438 ± 0.002	0.999	0.0007	5
3. Diethyl ketone	0.429 ± 0.002	0.999	0.0009	5
4. Carbon tetrachloride	0.268 ± 0.001	0.999	0.0003	5
5. Ethyl acetate	0.418 ± 0.002	0.999	0.0010	5
6. Cyclopentanone	0.431 ± 0.001	0.999	0.0006	5
7. Dioxane	0.503 ± 0.020	0.997	0.0090	5
8. Acetonitrile	0.271 ± 0.001	0.999	0.0003	5
9. Acetone	0.353 ± 0.001	0.999	0.0005	5
10. Methanol	0.299 ± 0.020	0.993	0.0090	5
11. Ethanol	0.360 ± 0.020	0.996	0.0080	5
12. Ethylene glycol	0.256 ± 0.001	0.999	0.0003	5
13. Dimethyl sulfoxide	0.396 ± 0.001	0.999	0.0003	5
14. Tetrahydrofuran	0.452 ± 0.002	0.999	0.0010	5

^a Reaction constant.^b Correlation coefficient.^c Standard deviation of the estimate.^d Number of points used in the calculation.

correct interpretation of the solvating effects on the carboxylic group in the selected solvent set. For these reasons, it is considered that the results presented in this work may be used to quantitatively estimate and separate the overall solvent effects into the contributions of the initial and the transition state in the reaction of diazodiphenylmethane with carboxylic acids. The solvation models for 2-(4-substituted phenyl)-cyclohex-1-enecarboxylic acids, 2-(4-substituted phenyl)-benzoic

Table X Hammett Reaction Constants for 2-(4-Substituted Phenyl)-acrylic Acids

Solvent	ρ^a	r^b	s^c	d^d
1. Methyl acetate	0.801 ± 0.002	0.999	0.0010	5
2. Cyclohexanone	0.852 ± 0.002	0.999	0.0009	5
3. Diethyl ketone	0.826 ± 0.002	0.999	0.0008	5
4. Carbon tetrachloride	0.516 ± 0.001	0.999	0.0006	5
5. Ethyl acetate	0.815 ± 0.003	0.999	0.0010	5
6. Cyclopentanone	0.836 ± 0.001	0.999	0.0006	5
7. Dioxane	0.923 ± 0.003	0.999	0.0010	5
8. Acetonitrile	0.528 ± 0.001	0.999	0.0007	5
9. Acetone	0.679 ± 0.002	0.999	0.0008	5
10. Methanol	0.580 ± 0.040	0.992	0.0190	5
11. Ethanol	0.643 ± 0.060	0.987	0.0270	5
12. Ethylene glycol	0.489 ± 0.001	0.999	0.0006	5
13. Dimethyl sulfoxide	0.767 ± 0.002	0.999	0.0009	5
14. Tetrahydrofuran	0.866 ± 0.002	0.999	0.0010	5

^a Reaction constant.^b Correlation coefficient.^c Standard deviation of the estimate.^d Number of points used in the calculation.

acids, and 2-(4-substituted phenyl)-acrylic acids are suggested. The results show that the presence of the substituted phenylene group at the C-2 position affects the orientation of the carboxylic group. The degree of these interactions is in agreement with the obtained kinetic data, solvation models, and characteristics of the examined carboxylic acid molecule.

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