

Solvent and Structural Effects on the Kinetics of the Reactions of 2-Substituted Cyclohex-1-enylcarboxylic and 2-Substituted Benzoic Acids with Diazodiphenylmethane

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ABSTRACT: The rate constants for the reaction of 2-methyl-cyclohex-1-enylcarboxylic, 2-phenylcyclohex-1-enylcarboxylic, and 2-methylbenzoic and 2-phenylbenzoic acids with diazodiphenyl-methane were determined in 14 various solvents at 30°C. 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 quantitative relationship between the molecular structure and the chemical reactivity has been discussed, as well as the effect of geometry on the reactivity of the examined molecules. The geometric data of all the examined compounds corresponding to the energy minima in solvent, simulated as dielectric continuum, obtained using semiempirical MNDO-PM3 energy calculations. © 2007 Wiley Periodicals, Inc. *Int J Chem Kinet* 39: 664–671, 2007

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INTRODUCTION

Previous studies [1–5] of the kinetics of the reaction of carboxylic acids with diazodiphenylmethane (DDM) in various solvents have revealed the important role of the nonspecific and specific solvent effects



on the reactivity. The examined reaction may vary in rate, depending on the reactants and conditions, but it usually follows the second-order kinetics [1,2]. The mechanism of this reaction has been thoroughly studied [6–9], and a spectrophotometric method and kinetic approaches have been developed [10,11]. It has been shown that the reactivity of carboxylic acids is influenced by the preferential solvation of the reactants and/or the transition state, through the nonspecific and specific solvent–solute interactions. Furthermore, it has been established that the multiple linear regression analysis may well be used to separate and quantify the impact of such solvent–solute interactions on reactivity [3].

This paper extends our work on the reactivity of α,β -unsaturated carboxylic acids in their reaction with DDM in various solvents [12–15]. It is a very important class of organic compounds, because they occur widely in nature and because these molecules have powerful biological properties and are the targets of the variety of synthetic approaches [16].

In general, the presence of an α,β -double bond in the ring of a cyclohex-1-enylcarboxylic acid increases the acid reactivity, due to the inductive effect of the unsaturated α -carbon atom. At the same time, the mesomeric effect of an α,β -double bond on the carboxylic group decreases the reactivity of the acid, as in the ground state the resonance interaction between the double bond and the carboxylic group stabilizes the acid; whereas in the case of the anion the resonance stabilization is mainly within the carboxylate ion itself, and the effect of a conjugate double bond is less significant [17] (Fig. 1). Our previous investigations [18] showed that the rate constant for the reaction of DDM with α,β -unsaturated acids in ethanol is higher than for the corresponding saturated compounds due to the effect of the polar and mesomeric factors, which oppose one another, indicating the predominance of the former one. The values of the rate constants for the correspond-

ing cycloalkenylacetic acids are still higher, which can be interpreted as the evidence of the influence of the mesomeric effect in the case of cycloalkenylcarboxylic acids [18]. In our previous work [12], we examined the reactivity of 2-substituted cyclohex-1-enylcarboxylic acids with DDM in various alcohols. The results have shown that the linear free energy relationships are applicable to the kinetic data for 2-substituted cyclohex-1-enyl-carboxylic system with the substituents of moderate steric bulkiness. Comparisons were made with the ortho-substituted benzoic acid system, under the same experimental conditions. The results have shown that there are slight differences in the composition of the electronic effects depending on the type of the double bond through which the effects are transmitted. Starting from the assumption on similarity of the polar interactions of the substituents with the reaction center and on proximity effects, these differences were ascribed to the different polarizability of the examined double bonds.

In the present work, the second-order rate constants have been measured for the reaction of 2-methylcyclohex-1-enylcarboxylic, 2-phenylcyclohex-1-enylcarboxylic, 2-methylbenzoic, and 2-phenylbenzoic acids with DDM in 14 various solvents at 30°C. Our objective was to investigate the influence of the solvents on the ortho-effect of the substituents in the systems subjected to the secondary steric effects of ortho-substituents. The solvent effects on the reaction rate constants were interpreted by means of the linear solvation energy relationships concept, developed by Kamlet and Taft [19], expressed in the following form:

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

where π^* , α , and β are solvatochromic parameters; s , a , and b are the complementary solute-dependent coefficients of the solvent parameters; and A_0 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

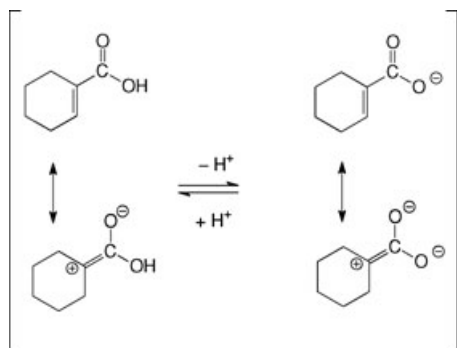


Figure 1 The mesomeric effect of an α,β -double bond on the carboxylic group in the ground state and in the anion.

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 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 quantitative relationship between the molecular structure and the chemical reactivity has been discussed, as well as the effect of geometry on the reactivity of the examined molecules. The geometric data of all the examined compounds corresponding to the energy minima in solvent were obtained using semiempirical MNDO-PM3 energy calculations.

MATERIALS AND METHODS

Cyclohex-1-enylcarboxylic, 2-methylcyclohex-1-enylcarboxylic, and 2-phenylcyclohex-1-enylcarboxylic acids were prepared by the method of Wheeler and Lerner [20], from the corresponding cyclohexanone cyanohydrine, which was dehydrated to cyanocyclohexene. Nitrile was hydrolyzed with phosphoric acid to the corresponding cyclohex-1-enylcarboxylic acid. Benzoic, 2-methylbenzoic, and 2-phenylbenzoic acids were commercial products (Fluka, Germany).

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

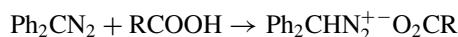
Diazodiphenylmethane was prepared by the method of Smith et al. [21], and stock solutions were stored in a refrigerator and diluted before use. Solvents were purified as described in previous papers [7,22]. All the solvents used in the kinetic studies were of analytical grade. Rate constants for the reaction of examined acids with DDM were determined as reported previously, by the spectroscopic method of Roberts and his coworkers [10], 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 the particular second-order rate constants agreed within 3% of the mean. The correlation analysis was carried out 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 geometries of all the molecular species examined in this work, corresponding to the energy minima

in solvent, were obtained using semiempirical MNDO-PM3 energy calculations [23,24].

RESULTS AND DISCUSSION

The second-order rate constants for the reaction of 2-methylcyclohex-1-enylcarboxylic, 2-phenylcyclohex-1-enylcarboxylic, 2-methylbenzoic, and 2-phenylbenzoic acids with DDM in 14 various solvents at 30°C , together with the previously determined [15] rate constants for cyclohex-1-enylcarboxylic and benzoic acids, are given in Tables I and II. Comparison of the rate constants in protic and aprotic solvents indicates that the examined reaction is slower in aprotic solvents, which are in accordance with the supposed reaction mechanism [6–9]. 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.



Our previous investigations of the reactivity of α,β -unsaturated carboxylic acids with DDM in various solvents [12–15] 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. 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.

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 equation (1). The solvent parameters, which were determined by Kamlet et al. [25], are given in Table III. The correlations obtained from the data given

Table I The Second-Order Rate Constants ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$) for the Reaction of Cyclohex-1-enylcarboxylic, 2-Methylcyclohex-1-enylcarboxylic, and 2-Phenylcyclohex-1-enylcarboxylic Acids with Diazodiphenylmethane at 30°C in a Set of Various Solvents

	Solvent	$k(\text{dm}^3 \text{mol}^{-1} \text{min}^{-1})$		
		Cyclohex-1-enylcarboxylic Acid	2-Methylcyclohex-1-enylcarboxylic Acid	2-Phenylcyclohex-1-enylcarboxylic Acid
1	Methyl acetate	0.032	0.093	0.068
2	Cyclohexanone	0.020	0.044	0.038
3	Diethylketone	0.053	0.064	0.133
4	Carbontetrachloride	0.329	0.359	0.873
5	Ethyl acetate	0.025	0.058	0.054
6	Cyclopentanone	0.025	0.053	0.049
7	Dioxane	0.065	0.077	0.142
8	Acetonitrile	0.318	0.420	0.839
9	Acetone	0.048	0.106	0.103
10	Methanol	0.818	0.762	2.790
11	Ethanol	0.417	0.264	1.279
12	Ethylene glycol	1.962	1.631	6.367
13	DMSO	0.008	0.013	0.014
14	Tetrahydrofuran	0.019	0.027	0.037

by Marcus [26] did not give satisfactory results. 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 correlation results obtained are as follows:
Cyclohex-1-enylcarboxylic acid

$$\log k = (-0.58 \pm 0.12) + (0.38 \pm 0.20)\pi^* + (2.07 \pm 0.09)\alpha - (2.48 \pm 0.21)\beta$$

$$(R = 0.990, s = 0.11, F = 168, n = 14)$$

2-Methylcyclohex-1-enylcarboxylic acid

$$\log k = (-0.49 \pm 0.10) + (0.52 \pm 0.16)\pi^* + (1.66 \pm 0.07)\alpha - (2.35 \pm 0.17)\beta$$

$$(R = 0.989, s = 0.09, F = 162, n = 14)$$

2-Phenylcyclohex-1-enylcarboxylic acid

$$\log k = (-0.14 \pm 0.08) + (0.35 \pm 0.22)\pi^* + (2.34 \pm 0.10)\alpha - (2.70 \pm 0.24)\beta$$

$$(R = 0.991, s = 0.13, F = 175, n = 14)$$

Table II The Second-Order Rate Constants ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$) for the Reaction of Benzoic, 2-Methylbenzoic and 2-Phenylbenzoic Acids with Diazodiphenylmethane at 30°C in a Set of Various Solvents

	Solvent	$k(\text{dm}^3 \text{mol}^{-1} \text{min}^{-1})$		
		Benzoic Acid	2-Methylbenzoic Acid	2-Phenylbenzoic Acid
1	Methyl acetate	0.260	0.124	0.316
2	Cyclohexanone	0.220	0.129	0.246
3	Diethylketone	0.265	0.157	0.268
4	Carbontetrachloride	0.638	0.389	1.010
5	Ethyl acetate	0.180	0.094	0.236
6	Cyclopentanone	0.293	0.145	0.338
7	Dioxane	0.058	0.035	0.110
8	Acetonitrile	3.730	1.590	5.500
9	Acetone	0.350	0.152	0.400
10	Methanol	2.470	1.860	11.61
11	Ethanol	0.995	0.933	5.000
12	Ethylene glycol	4.020	2.590	15.37
13	DMSO	0.141	0.079	0.162
14	Tetrahydrofuran	0.105	0.060	0.147

Table III Solvent Parameters [24]

	Solvent	π^*	α	β
1	Methyl acetate	0.60	0.00	0.42
2	Cyclohexanone	0.76	0.00	0.53
3	Diethylketone	0.72	0.00	0.45
4	Carbontetrachloride	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	DMSO	1.00	0.00	0.76
14	Tetrahydrofuran	0.58	0.00	0.55

Benzoic acid

$$\log k = (-0.64 \pm 0.28) + (1.34 \pm 0.47)\pi^* \\ + (1.51 \pm 0.22)\alpha - (1.98 \pm 0.49)\beta \\ (R = 0.915, s = 0.26, F = 17, n = 14)$$

2-Methylbenzoic acid

$$\log k = (-0.83 \pm 0.27) + (1.05 \pm 0.44)\pi^* \\ + (1.64 \pm 0.20)\alpha - (1.75 \pm 0.46)\beta \\ (R = 0.932, s = 0.25, F = 22, n = 14)$$

2-Phenylbenzoic acid

$$\log k = (-0.34 \pm 0.26) + (0.99 \pm 0.41)\pi^* \\ + (2.11 \pm 0.19)\alpha - (1.90 \pm 0.44)\beta \\ (R = 0.961, s = 0.24, F = 40, n = 14).$$

From all the above equations, it can be concluded that the solvent effects influence the carboxylic acid-DDM reaction by two reverse effects. The opposite signs of the electrophilic and the nucleophilic parameters are 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 dominate the transition state and increase the reaction rate, and the negative sign of the b coefficient points out that HBA effects stabilize the initial state before the reaction starts and are responsible for a decrease in the reaction rate. From the values of regression coefficients, the contribution of each parameter to

Table IV The Percentage Contributions of Kamlet-Taft's Solvatochromic Parameters to the Reactivity

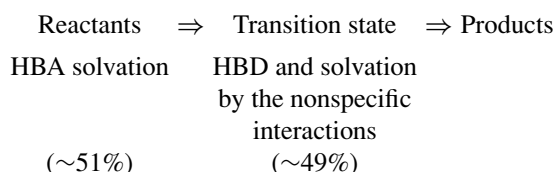
	Compound	$P\pi^*$ (%)	$P\alpha$ (%)	$P\beta$ (%)
1	Cyclohex-1-enylcarboxylic acid	8	42	50
2	2-Methylcyclohex-1-enylcarboxylic acid	11	37	52
3	2-Phenylcyclohex-1-enylcarboxylic acid	7	43	50
4	Benzoic acid	28	31	41
5	2-Methylbenzoic acid	24	37	39
6	2-Phenylbenzoic acid	20	42	38

reactivity, on a percentage basis, was calculated and is listed in Table IV. From these results it can be noticed that the nonspecific interactions (π^*) are less pronounced than the specific (α, β). However, the specific interactions have more influence on the cyclohexenyl systems (87%–93%) than on benzoic systems (72%–80%). It probably means the carboxyl group of the cyclohexenyl acids is more susceptible to the proton-donor and proton-acceptor solvent effects than the carboxyl group of benzoic acids.

The π^* term is needed to account for the observed rate enhancing effect of the behaviour of a solvent as a dielectric (all the applied solvents have significant π^* values, Table III). In this work, the π^* term is statistically insignificant in equations for 2-substituted cyclohex-1-enylcarboxylic acids; however, for benzoic acids, it has an influence of 20%–28%, which is too high to neglect it. The removal of π^* parameter decreases the reliability of the Kamlet-Taft model and makes it incomplete, because it can cause the reversal of arithmetic signs in front of the parameters and the drop of the correlation coefficient (R) to about 0.80. Therefore, the authors suggest that π^* should remain included in the mentioned equations.

To get a complete view of the solvent interactions with the molecules of the examined carboxylic acids, the solvent effects are expressed quantitatively, for both acid systems and referring separately to the ground and the transition state.

2-Substituted cyclohex-1-enylcarboxylic acid system:



2-Substituted benzoic acid system:

Reactants	⇒	Transition state	⇒	Products
HBA solvation (~39%)		HBD and solvation by the nonspecific interactions (~61%)		

The suggested solvation models indicate that the 2-substituted cyclohex-1-enylcarboxylic acid system is more sensitive to the HBA solvent interactions than the 2-substituted benzoic acid system (Table IV) and less sensitive to the HBD solvent ability. However, the more general conclusion that comes from these results is that the substituents at the C-2 position in both carboxylic acid types have very weak influence on the solvation effects during the reaction with DDM.

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 and benzoic acids. Such a conclusion can be drawn from the minimal energy molecular conformations. The geometric data of all the examined acids corresponding to the energy minima in solvent were obtained using the semiempirical MNDO-PM3 energy calculations (including COSMO facility in it) and are shown in Figs. 2–7 and Table V.

In the molecule of benzoic acid, the carboxylic group is almost planar with the ring (Fig. 2), which is a cause of the conjugation of the carbonyl group of the carboxylic group and the benzene ring. In the case of cyclohex-1-enylcarboxylic acid (Fig. 3), the carboxylic group is 142° twisted out of the plane of the double bond and of the opposite orienta-

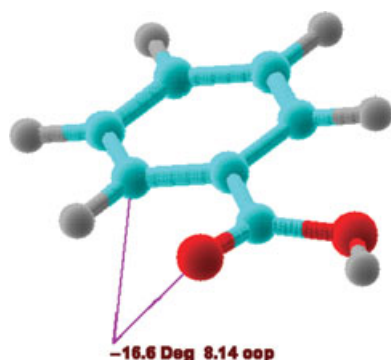


Figure 2 The most stable conformation of benzoic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

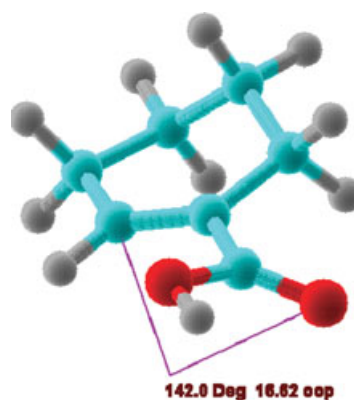


Figure 3 The most stable conformation of cyclohex-1-enylcarboxylic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

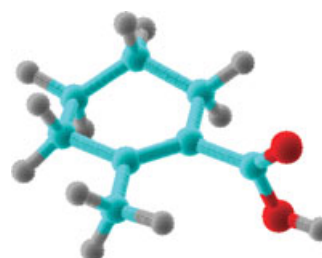


Figure 4 The most stable conformation of 2-methylcyclohex-1-enylcarboxylic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

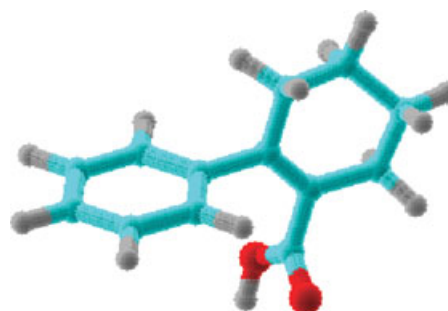
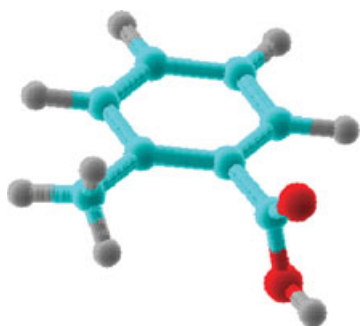
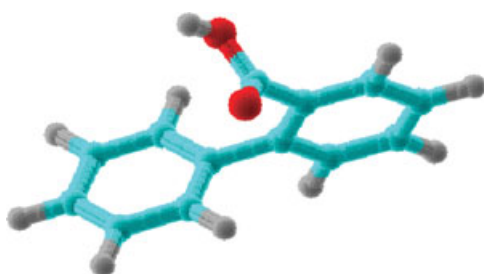


Figure 5 The most stable conformation of 2-phenylcyclohex-1-enylcarboxylic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion comparing to benzoic acid. The double bond of cyclohex-1-enylcarboxylic acid is much nearer to the carboxylic group, which can have as a consequence 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. The torsion angles between the carboxylic group and the C-2 atom

Table V Data Calculated Using Semiempirical MNDO-PM3 Method

	Compound	Torsion Angle (°)	Heat of Formation (kcal mol ⁻¹)
1	Cyclohex-1-enylcarboxylic acid	142.0	-94.97
2	2-Methylcyclohex-1-enylcarboxylic acid	-93.30	-103.1
3	2-Phenylcyclohex-1-enylcarboxylic acid	-94.10	-68.23
4	Benzoic acid	-16.60	-66.27
5	2-Methylbenzoic acid	-87.50	-73.78
6	2-Phenylbenzoic acid	92.50	-38.86

**Figure 6** The most stable conformation of methylbenzoic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]**Figure 7** 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.]

are given in Table V for all the examined acids, together with the corresponding conformation energies. The conformations with the minimal energy contents for the other four examined acids are given in Figs. 3–6.

The presence of the methyl group at ortho-position causes the increase in the heat of formation of the compound, which is in fact the energy content of the most stable conformation. The presence of the phenyl group at ortho-position of both benzoic and cyclohex-1-enylcarboxylic acid significantly decreases the energy content of the compound, which points to the high extent of conjugation between the double bond in the cyclohexene ring and the phenyl group, or between two phenyl groups, and therefore to the absence of the ortho-effect for these phenyl-substituted acids.

Generally, the presence of the substituent affects the orientation of the carboxylic group (torsion angles), comparing to the unsubstituted molecules, but the secondary steric effect is obviously of little or no significance in these systems. The electronic effect of substituents is dominant in both systems of the examined carboxylic acids in the reaction with DDM.

CONCLUSION

On the basis of the results presented in this work and our previously reported results for more than 50 carboxylic acids, it can be concluded that the solvatochromic concept of Kamlet and Taft is applicable to 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-enylcarboxylic and 2-substituted benzoic acids are suggested. The results show that the substituents at the C-2 position of the ring have rather a weak influence on the solvation effects during the reaction of carboxylic acids with DDM. For these reasons, we consider that the results presented in this work may be used to quantitatively estimate and separate the overall solvent effects into initial and transition state contributions in the reaction of DDM with carboxylic acids.

The reactivity of the examined carboxylic acids in the reaction with DDM is in agreement with the geometric characteristics obtained using the semiempirical MNDO-PM3 energy calculations.

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