The reactivity of α,β-unsaturated carboxylic acids. Part XVI. The kinetics of the reaction of cycloalkenylcarboxylic and cycloalkenylacetic acids with diazodiphenylmethane in various alcohols

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The rate constants for the reaction of diazodiphenylmethane with 1-cyclopentene-carboxylic, 1-cycloheptene-carboxylic, cyclopent-1-enylacetic and cyclohept-1-enylacetic acids were determined in eight alcohols at 30 ºC using the appropriate UV-spectroscopic method. In order to explain the kinetic results through solvent effects, the second order rate constants of the examined acids were correlated using a total solvatochromic equation, of the form: \( \log k = A_0 + s\pi^\alpha + b\beta \), where \( \pi^\alpha \) is a measure of the solvent polarity, \( \beta \) represents the scale of solvent hydrogen bond acceptor basicities and \( \alpha \) represents the scale of solvent hydrogen bond donor acidities. The correlations of the kinetic data were carried out by means of multiple linear regression analysis. The opposite sings of the electrophilic and the nucleophilic parameters are in agreement with the well-known reaction mechanism. The results presented in this paper were compared with the kinetic data for 1-cyclohexene-carboxylic and cyclohex-1-enylacetic acids obtained under the same experimental conditions.

Keywords: cycloalkenecarboxylic acids, cycloalkenylacetic acids, diazodiphenyl-methane, kinetic measurements, protic solvents.

INTRODUCTION

The relationship that exists between the structure of carboxylic acid and their reactivity with diazodiphenylmethane (DDM) has been studied by many authors with particular regard to the influence of the solvent. This paper extends our work on the reactivity of cycloalkenecarboxylic and cycloalkenylacetic acids in their reaction with DDM in various alcohols. In general, the presence of and α,β-double bond in the ring of a cycloalkenylcarboxylic acid increases the acid strength, due to the inductive effect of the α-carbon atom. In addition, the electronegativity of this atom is increased by the strain that is introduced into the ring by the presence of the double bond. This

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strain decreases with the number of ring carbon atoms leading to lower rate constants. At the same time the mesomeric effect of the \(\alpha,\beta\)-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, while in the case of the anion the resonance stabilization is mainly within the carboxylate ion itself, and the effect of the conjugate double bond is less significant.\(^7\) Previous investigations\(^3\) showed that the rate constant for the reaction of DDM with 1-cyclopentencarboxylic and 1-cycloheptencarboxylic acids in ethanol are higher than for the corresponding saturated compounds due to “net effect” of polar and mesomeric factors, which oppose one another, indicating the predominance of the former one. The values of the rate constants for the corresponding cycloalkenylacetic acids are still higher, which can be interpreted as evidence of the influence of the mesomeric effect in case of cycloalkencarboxylic acids.\(^3\)

In the present work, rate constants were determined at 30 °C for the reaction of 1-cyclopentencarboxylic, 1-cycloheptencarboxylic, cyclopent-1-enylacetic and cyclohept-1-enylacetic acids with DDM in eight different alcohols. By comparison of the obtained results with the results for 1-cyclohexencarboxylic, and cyclohex-1-enylacetic acid, determined previously,\(^4,5\) the effect of the \(\alpha,\beta\)-double bond, as well as of the ring size on the reactivity of the examined carboxylic acids in different alcohols is discussed. The effect of solvent polarity and hydrogen bonding on the rate constants is interpreted by means of the linear solvation energy relationships (LSER) concept, developed by Kamlet and Taft\(^8\) using the general solvatochromic equation, of the form:

\[
\log k = A_0 + s\pi^* + a\alpha + b\beta
\]  

(1)

where \(\alpha, \beta\) and \(\pi^*\) are solvatochromic parameters, \(a, b,\) and \(s\) are solvatochromic coefficients and \(A_0\) is the regression value of the solute property in the reference solvent, cyclohexane.

In Eq. (1) \(\pi^*\) is the index of the solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole ty its own dielectric effects. The \(\pi^*\) scale was selected to run from 0.00 for cyclohexanone to 1.00 for dimethylsulfoxide. The \(\alpha\) coefficient represents the solvent hydrogen bond donor (HBD) acidity, in other words it describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The \(\alpha\) scale extends from 0.00 for non-HBD solvents to about 1.00 for methanol. The \(\beta\) coefficient is a measure of a solvent hydrogen bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton in a solute-to-solvent hydrogen bond. The \(\beta\) scale was selected to extend from 0.00 for non-HBA solvents to about 1.00 for hexamethylphosphoric acid triamide.

Aslan, Collier and Shorter\(^2\) showed that correlation analysis of second-order rate constants for the reaction of benzoic acid with DDM in hydroxylic solvents does not give satisfactory results with the Koppel-Palm analysis. They came to the conclusion that the possibility of a Koppel-Palm analysis of data related to protic solvents depends on the fitting of the data in a regression with the main lines being determined by a much larger number of aprotic solvents. The influence of hydrophilic solvents on the reactivity of carboxylic acids with DDM by Kamlet-Taft treatment has not been systematically
presented before. The correlation equations for 1-cyclohexenecarboxylic and benzoic acids in alcohols given in our previous paper\(^9\) are not relevant because of the inappropriate choice of the \(\beta\) solvent parameter.

In this work the correct correlation analysis by one, two or three parameter correlation, involving the logarithams of the rate constants is presented. The present paper demonstrates how the linear solvation energy relationship method can be used to unravel, quantify, correlate and rationalize multiple interacting effects of the solvent on the reactivity parameters of cycloalkenylcarboxylic and cycloalkenylacetic acids in their reaction with DDM.

**RESULTS AND DISCUSSION**

The second-order rate constants for the reaction for cyclopent-1-enylcarboxylic, 1-cycloheptenecarboxylic, cyclopent-1-enylacetic and cyclohept-1-enylacetic acids with DDM in various alcohols at 30 ºC, together with the previously determined\(^4,5,9\) the rate constants for cyclohex-1-enylcarboxylic and cyclohex-1-enylacetic acids, are given in Tables I and II.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1-Cyclopentenecarboxylic acid</th>
<th>1-Cyclohexenecarboxylic acid(^a)</th>
<th>1-Cycloheptenecarboxylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1.106</td>
<td>0.818</td>
<td>0.654</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.534</td>
<td>0.417</td>
<td>0.332</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>0.653</td>
<td>0.503</td>
<td>0.388</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>0.381</td>
<td>0.376</td>
<td>0.355</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>0.556</td>
<td>0.478</td>
<td>0.364</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>0.345</td>
<td>0.339</td>
<td>0.275</td>
</tr>
<tr>
<td>2-Methylpropan-2-ol</td>
<td>0.298</td>
<td>0.220</td>
<td>0.184</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>2.452</td>
<td>1.962</td>
<td>1.570</td>
</tr>
</tbody>
</table>

\(^a\)Rate constants determined previously.\(^4,9\)

The results (Tables I and II) show that the values of the rate constants grow with increasing solvent polarity. This is in accordance with the suggested mechanism of the reaction between carboxylic acids and DDM which involves the rate determining proton transfer from the acid to DDM to form a diphenylmethanediazonium carboxylate ion pair.\(^10,11\)

\[ \text{Ph}_2\text{CH}_2 + \text{RCOOH} \rightarrow \text{Ph}_2\text{CHN}_2^+ \cdot \text{OOCR} \]

It is interesting to compare the differences in the rate constants for the examined acids because the effects of strain due to the endocyclic double bond are responsible for the prominent changes in the reactivity of the acids. The presence of a double bond in a five-membered ring leads to "tension" in the system, which is relieved in a six-membered ring, for example, by the folding of the molecule into the "half-chair" conforma-
tion – a similar effect in a five-membered is not possible. It was found that cyclopentenyl acids have higher rate constants than the corresponding cyclohexenyl acids (Tables I and II). 1-Cycloheptenecarboxylic and cyclohept-1-enylacetic acids have slightly lower rate constants than the other two mentioned acid systems, which is probably due to the fact that even the slight strain present in the cyclohexenyl acid systems is absent in the larger seven-membered rings.

### TABLE II. Rate constants (dm$^3$mol$^{-1}$min$^{-1}$) for the reaction of cyclopent-1-enylacetic, cyclohex-1-enylacetic, and cyclohept-1-enylacetic acids with DDM at 30 ºC in various alcohols

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Cyclopent-1-enylacetic acid</th>
<th>Cyclohex-1-enylacetic acid</th>
<th>Cyclohept-1-enylacetic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.236</td>
<td>1.652</td>
<td>1.300</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.828</td>
<td>0.659</td>
<td>0.614</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>0.796</td>
<td>0.762</td>
<td>0.748</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>0.452</td>
<td>0.446</td>
<td>0.421</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>0.806</td>
<td>0.694</td>
<td>0.528</td>
</tr>
<tr>
<td>Butan-2-ol</td>
<td>0.431</td>
<td>0.424</td>
<td>0.343</td>
</tr>
<tr>
<td>2-Methylpropan-2-ol</td>
<td>0.164</td>
<td>0.140</td>
<td>0.132</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>4.080</td>
<td>3.020</td>
<td>2.237</td>
</tr>
</tbody>
</table>

*Rate constants determined previously.*

The rate constants for the cycloalkenylacetic acids (Table II) in all the used solvents were higher than the rate constants for the cycloalkenylcarboxylic acids in the corresponding alcohols. This is in accordance with the fact that the resonance interaction between the double bond and the carbonyl group in the cycloalkenylcarboxylic acids causes a decrease in the acid strength.

In earlier papers, correlation analysis of the second order rate constant – solvent properties relation were presented for the reaction of 1-cyclohexenecarboxylic and cyclohex-1-enylacetic acid with diazodiphenylmethane at 30 ºC in various alcohols. It was concluded that the solvent effect is best expressed through multiple regression of log $k$ with $f(e)$ (the Kirkwood function of dielectric constant $e/(2e + 1)$), $\sigma^*$ (the Taft polar constant for the alkyl group of the alcohol) and $n_{\gamma H}$ (the number of $\gamma$-hydrogen atoms in the alcohol). The favourable influence of the dielectric constant was expected for the reaction in which the route from the initial to the transition state involves charge separation, but the stepwise regression showed that the $\sigma^*$ term is more important. This indicated the dominant role of the solvating properties of the alcohol, i.e., Lewis basicity or acidity of the solvent.

In order to explain the obtained kinetic results through solvent polarity and basicity or acidity, the reaction rate constants of the examined acids were correlated with solvent properties using the total solvatochromic Eq. (1). The solvent parameters are shown in Table III. The correlations of the kinetic data were carried out by means of multiple linear regression analysis.
### TABLE III. Solvent parameters for alcohols.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\pi$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.60</td>
<td>0.93</td>
<td>0.62</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.54</td>
<td>0.83</td>
<td>0.77</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>0.52</td>
<td>0.78</td>
<td>0.83</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>0.48</td>
<td>0.76</td>
<td>0.95</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>0.47</td>
<td>0.79</td>
<td>0.88</td>
</tr>
<tr>
<td>2-Methylpropan-2-ol</td>
<td>0.41</td>
<td>0.68</td>
<td>1.01</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.92</td>
<td>0.90</td>
<td>0.52</td>
</tr>
</tbody>
</table>

*Values are available for only seven alcohols.

Regression analysis of $\log k$ on $\pi^*$, $\alpha$ and $\beta$ solvent parameters gave poor results for all the examined acids. The Eqs. (2a) – (2f) below involve analysis by partial regressions for cyclopent-1-enylcarboxylic acid in seven alcohols.

1. \[
\log k = 0.16 + (0.65 \times 0.54)\pi^* + (0.99 \times 1.78)\alpha - (0.995 \times 1.26)\beta \\
R = 0.981, s = 0.083, n = 7
\]

2. \[
\log k = -1.02 + (1.48 \times 0.25)\pi^* \\
R = 0.935, s = 0.17, n = 7
\]

3. \[
\log k = -2.67 + (3.08 \times 0.82)\alpha \\
R = 0.860, s = 0.91, n = 7
\]

4. \[
\log k = 1.16 - (1.68 \times 0.21)\beta \\
R = 0.960, s = 0.091, n = 7
\]

5. \[
\log k = -1.93 + (1.03 \times 0.23)\pi^* + (1.43 \times 0.53)\alpha \\
R = 0.977, s = 0.08, n = 7
\]

6. \[
\log k = -0.31 + (0.63 \times 0.31)\pi^* - (1.06 \times 0.36)\beta \\
R = 0.981, s = 0.072, n = 7
\]

The correlation coefficients and the standard deviations in the multiple parameter model given by Eq. (2a) are not so unreliable but the regression coefficients of $\pi^*$, $\alpha$ and $\beta$, are irrelevant as they display appreciable standard errors which may change the course of interaction. The best results were obtained by two-parameter models as shown by Eqs. (2e) and (2f).

The correlation equations developed by stepwise regression for all the examined acids showed that the best approach by which to understand the hydroxylic solvent effects in this reaction lies in the separate correlations of the kinetic data with the hydrogen-bond donating (HBD) and hydrogen-bond accepting (HBA) ability of a solvent.
The correlation results obtained for all the other acids included in this research are given in the set of Eqs. 3–7.

1-Cyclohexenecarboxylic acid:

\[
\log k = -1.92 + (1.05 \pm 0.23)\pi^* + (1.30 \pm 0.52)\alpha \\
R = 0.977, s = 0.077, n = 7
\]  
(3a)

\[
\log k = -0.06 + (0.79 \pm 0.38)\pi^* - (0.83 \pm 0.43)\beta \\
R = 0.970, s = 0.089, n = 7
\]  
(3b)

1-Cycloheptenecarboxylic acid:

\[
\log k = -1.91 + (1.06 \pm 0.22)\pi^* + (1.16 \pm 0.51)\alpha \\
R = 0.977, s = 0.070, n = 7
\]  
(4a)

\[
\log k = -0.35 + (0.98 \pm 0.48)\pi^* - (0.66 \pm 0.44)\beta \\
R = 0.960, s = 0.090, n = 7
\]  
(4b)

Cyclopent-1-enylacetic acid:

\[
\log k = -3.56 + (0.80 \pm 0.33)\pi^* + (3.74 \pm 0.75)\alpha \\
R = 0.980, s = 0.110, n = 7
\]  
(5a)

\[
\log k = 1.91 - (2.47 \pm 0.31)\beta \\
R = 0.963, s = 0.133, n = 7
\]  
(5b)

Cyclohex-1-enylacetic acid:

\[
\log k = -3.33 + (0.75 \pm 0.41)\pi^* + (3.91 \pm 0.94)\alpha \\
R = 0.960, s = 0.140, n = 7
\]  
(6a)

\[
\log k = 1.66 - (2.26 \pm 0.36)\beta \\
R = 0.940, s = 0.150, n = 7
\]  
(6b)

Cyclohept-1-enylacetic acid:

\[
\log k = -3.12 + (0.67 \pm 0.42)\pi^* + (3.13 \pm 0.96)\alpha \\
R = 0.950, s = 0.140, n = 7
\]  
(7a)

\[
\log k = 1.44 - (2.06 \pm 0.35)\beta \\
R = 0.930, s = 0.150, n = 7
\]  
(7b)

From all the equations above it can be concluded that protic solvents influence the carboxylic acid–DDM reaction by two reverse effects. The opposite signs of the electrophilic and nucleophilic parameters are in accordance with the described mechanism. Classical solvation (\(\pi^*\)) and HBD effects (\(\alpha\)) dominate the transition state and increase the reaction rate (shown in the equations by the positive signs) but HBA effects (\(\beta\)) stabilize the initial state before the reaction commences and are responsible for a decrease of the reaction rate (negative sign).

The correlation equations developed by stepwise regression for cycloalke

1-ethylcarboxylic acids are slightly different than the equations obtained for cycloalke-
nylacetic acids. The best results for the latter group of acids were obtained by correlating log $k$ values separately with $\pi^*$ and $\alpha$ parameters, and $\beta$ only, without $\pi^*$, suggesting that the initial state of the reaction is influenced by hydroxylic solvents more prominently by HBA than by classical solvation effects.

Similar results were obtained by correlating literature kinetic data for benzoic and phenylacetic acid, given in Eqs. (8) and (9).

Benzoic acid:

$\log k = -2.87 + (0.83 \pm 0.36)\pi^* + (3.02 \pm 0.73)\alpha$

$R = 0.975, s = 0.103, n = 7$ (8a)

$\log k = 1.69 - (2.07 \pm 0.29)\beta$

$R = 0.954, s = 0.124, n = 7$ (8b)

$\log k = -2.48 + (0.85 \pm 0.31)\pi^* + (2.59 \pm 0.71)\alpha$

$R = 0.972, s = 0.105, n = 7$ (9a)

$\log k = 1.70 - (1.99 \pm 0.27)\beta$

$R = 0.950, s = 0.120, n = 7$ (9b)

The relationship between the ring size and the solvent polarity and hydrogen bonding effects shows that the same solvent properties influence the reaction of cycloalkenylcarboxylic acids with DDM in alcohols. The same relationship was obtained for cycloalkenylacetic acids. The results of the correlations given above show that the cycloalkenylacetic acid system is more sensitive to the HBD and HBA ability of the solvent than the cycloalkenylcarboxylic acid systems. This was confirmed by the smaller values of the $\pi^*$ and $\beta$ coefficients in the sets of Eqs. (2), (3) and (4). These differences are less prominent between benzoic and phenylacetic acids.

The results presented in this paper indicate that the influence of hydroxylic solvents on the rate constants of the reaction between carboxylic acids and DDM is rather complex. In these amphiprotic solvents, complications can be caused by self-association type -AB hydrogen bonding, and multiple type -A and type -B interactions. In type - A hydrogen bonding, the solute acts as HBA base and the solvent as a HBD acid. In type - B hydrogen bonding, the roles are reversed. Type - AB represents hydrogen bonding where the solute acts as both HBD acid and HBA base, associating with at least two molecules of amphiprotic solvent in a probably cyclic complex. In this work obtained satisfactory results of the correlations of the kinetic data of the examined acids by Kamlet-Taft equations with separate HBD and HBA abilities of the solvent indicate that the selected model was correct. This means that this model gives a detailed interpretation of the solvating effects of the carboxylic group in different hydroxylic solvents. In these circumstances where both the solvent and the solute are hydrogen bond donors it has been proven that it is quite difficult to untangle solvent dipolarity/polarizability, type - B hydrogen bonding and variable self-association effects from the usual multiple type -A hydrogen bonding interactions. For these reasons we consider that the results presented in this work may be utilized to separate and quantitatively estimate the effects of both hydrogen bonding types and solvent dipolarity.
EXPERIMENTAL

Materials

1-Cyclopentenecarboxylic acid, m. p. 121 ºC (Ref. 15), 1-cyclohexenecarboxylic acid m. p. 38 ºC (Ref. 16) and 1-cycloheptenecarboxylic acid m. p. 50 ºC (Ref. 17) were prepared by the method of Wheleer and Lerner18 from the corresponding cycloalkanone cyanhydrine which was dehydrated to cyanoalkene. The nitrile was hydrolyzed with phosphoric acid to the corresponding cycloalkene-carboxylic acid.

Cyclopent-1-enylacetic acid, b. p. 128–130 ºC (20 mbar),19 cyclohex-1-enylacetic acid, b. p. 138–140 ºC (14.6 mbar)20 and cyclohept-1-enylacetic acid, b. p. 153 ºC (22.6 mbar)21 were prepared by the method of Sugasawa and Saito22 from the corresponding ketone with ammonium acetate and the resulting cycloalkenylacetonitrile was hydrolyzed to the acid with potassium hydroxide.

Diazodiphenylmethane was prepared by the method of Smith and Howard,23 Stock solutions of 0.06 mol dm-3 were stored in a refrigerator and diluted before use in an appropriate solvent.

All the applied chemicals were of p. a. purity. The solvents were purified as described in literature.10

Kinetic measurements

The second-order rate constants for the reaction of cycloalkenylcarboxylic and cycloalkenyl-acetic acids with DDM were determined as previously reported by the spectroscopic method of Roberts and his co-workers24 using a UV-Shimatzu 160 A spectrophotometer. Optical density measurements were performed at 525 nm with 1 cm cells at 30±0.5 ºC.

The second-order rate constants for all the examined acids were obtained by dividing the pseudo-first-order rate constants by the acid concentration (the acid concentration was 0.06 mol dm-3 and of DDM 0.006 mol dm-3). Three to five rate determinations were made for each acid and in each case the individual second-order constant agreed to within 3 % of the mean.

IZVOD

РЕАКТИВНОСТ α,β-НЕЗАСИБЕНИХ КИСЕЛИНА. ДЕО XVI. КИНЕТИКА РЕАКЦИЈЕ ЦИКЛОАЛКениЛКАРБОНСКИХ И ЦИКЛОАЛКениЛСИРБЕТЕНИХ КИСЕЛИНА СА ДИАЗОДИФЕНИЛМЕТАНОМА У РАЗЛИЧИТИМ АЛКОХОЛИМА

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Константе брзина за реакцију између диазодифенилметана (DDM) и 1-циклопентенилкарбонске, 1-циклопентенкарбонске, циклопент-1-енсирбитне и циклопент-1-енилсирбитне киселине су одређене у осам алкохолних раствараца на 30 ºC одговарајућим UV-спектротометријским методом. Да би се добили кинетички резултати објашњили кроз ефекте раствараца константе брзина реакције (k) су корелисане тоталном солватохромном једначином облика: \[ \log k = A_0 + x\pi^* + ax + b\beta \], где је \( \pi^* \) мера полярности раствараца, \( \beta \) представља скалу базности раствараца као акцептора протона у водној вези, а \( \alpha \) скалу киселиности раствараца као донора протона у водној вези. Корелација кинетичких параметара је извршена методом вишеструке линеарне регресионе анализе. Супротни знаци уз електрофилни и нуклеофилни параметар у сагласности су са изведеним механизом реакције. Резултати прикључени у овом раду су упоређени са кинетичким подацима за 1-циклопентенкарбонску и циклопекс-1-енилсирбитну киселину, добијеним под истим експерименталним условима.

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REFERENCES: