

Solvent effect on electronic absorption spectra of cyclohex-1-enylcarboxylic and 2-methylcyclohex-1-enylcarboxylic acids *

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The ultraviolet absorption spectra of cyclohex-1-enylcarboxylic acid and 2-methylcyclohex-1-enylcarboxylic acid were determined in six protic and nine aprotic solvents in the wavelength range from 200 to 400 nm. The position of the λ_{\max} of the two examined acids showed that the ultraviolet absorption maximums of cyclohex-1-enylcarboxylic acid were at consistently longer wavelengths in protic solvents than those of methylcyclohex-1-enylcarboxylic acid. The opposite was true in aprotic solvents. In order to explain the obtained results, the ultraviolet absorption frequencies of the electronic transitions in the carboxy carbonyl group of the examined acids were correlated using a total solvatochromic equation of the form: $\nu = \nu_0 + s\pi^* + a\alpha + b\beta$, where π^* is a measure of the solvent polarity, β represents the scale of solvent hydrogen bond acceptor basicities and α represents the scale of solvent hydrogen bond donor acidities. The correlation of the spectroscopic data was carried out by means of multiple linear regression analysis. The opposing solvent effects on the ultraviolet absorption maximums of the two examined acids were discussed.

Keywords: cyclohex-1-enylcarboxylic acid, 2-methylcyclohex-1-enylcarboxylic acid, ultraviolet absorption maximum, protic and aprotic solvents.

INTRODUCTION

The connection that exists between the structure and the ultraviolet absorption spectra of α , β -unsaturated acids has been studied by many authors.^{1,2} A number of authors^{3,4} have reviewed and critically examined the correlation of substituent constants with ultraviolet absorption frequencies. They observed that the correlation presents difficulties, both in interpretation and accuracy of measurement. In our previous works,^{5,6} it was shown that a clear linear relation between the position of the absorption bands for the electronic transitions of the carbonyl group of α , β -unsaturated acids in alcohols and the Taft's substituent constants exists.

In the present work, the ultraviolet absorption spectra of cyclohex-1-enylcarboxylic acid and 2-methylcyclohex-1-enylcarboxylic acid were recorded in six

* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday

protic and nine aprotic solvents. The effects of solvent polarity and hydrogen bonding on the absorption spectra are interpreted by means of the linear solvation energy relationships (LSER) concept, developed by Kamlet and Taft,⁷ using a general solvatochromic equation, of the form:

$$\nu_{\max} = \nu_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

where α , β and π^* are solvatochromic parameters and s , a and b are solvatochromic coefficients.

In Eq. (1), π^* 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 by its own dielectric effects. The π^* scale was selected to range from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide. The α 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 α scale extends from 0.00 for non-HBD solvents to about 1.00 for methanol. The β coefficient is a measure of the 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 β scale was selected to extend from 0.00 for non-HBD solvents to about 1.00 for hexamethylphosphoric acid triamide.

RESULTS AND DISCUSSION

In order to explain the difference in the influence of protic and aprotic solvent on cyclohex-1-enylcarboxylic acid and 2-methylcyclohex-1-enylcarboxylic acid, their UV spectra in a number of protic and aprotic solvents were recorded, as well as those of benzoic acid, for comparison. The absorption maximums are given in Table I and Table III.

A characteristic of the above mentioned UV spectra is the $n \rightarrow \pi^*$ electronic transition in the carbonyl group. In fact, during the excitation process one n electron is promoted from a nonbonding orbital on the oxygen to an antibonding orbital delocalized over the carbonyl group. Removal of an electron from the oxygen atom causes a decrease or even a reversal of the dipole moment – due to the presence of the mesomeric structure in the excited (transition) state: $>C^- - O^+$, which is the opposite of the charge disposition in the ground state. This dipole diminution corresponds to a *hypsochromic* shift (decrease of λ_{\max}) of the $n \rightarrow \pi^*$ absorption band with increasing solvent polarity.

It can be noticed from Table I that in protic solvents – alcohols – the wavelengths of the absorption maxima (λ_{\max}) of benzoic acid are much longer than those of the two cyclohexenyl acids, which is in accordance with its aromatic structure (high conjugation of electrons in the ring).

The wavelengths of the cyclohexenyl acids are considerably shorter, signifying higher absorption frequencies ($\nu_{\max} = 1/\lambda_{\max}$) and also the higher energy of the

$n \rightarrow \pi^*$ transition. The slightly shorter wavelength maximum of 2-methylcyclohex-1-enylcarboxylic acid than those of cyclohex-1-enylcarboxylic acid in alcohols denote an even higher energy of the electronic transition in the carbonyl group of the methyl-substituted acid. An explanation of the given facts could lay in the solvation of the ground and the transition state, complicated in the presence of the methyl group in the *ortho*-position.

TABLE I. Absorption maxima of the acids in various alcohols

Solvent	λ_{\max}/nm		
	Benzoic acid	Cyclohex-1-enylcarboxylic acid	2-Methylcyclohex-1-enylcarboxylic acid
Methanol	279.0	217.2	216.8
Ethanol	279.2	217.8	217.0
Propan-2-ol	279.4	216.2	216.0
Butanol	279.4	216.6	216.2
<i>t</i> -Butanol	279.6	217.4	217.2
Ethylene glycol	280.0	219.2	218.6

The mentioned $n \rightarrow \pi^*$ transition may be supported by the solvent, but it does not necessarily occur, which is shown by the correlation for each of the three acids in alcohols using equation (1).

The correlation of the spectroscopic data was carried out by means of multiple linear regression analysis. The solvent parameters are shown in Table II.

TABLE II. Solvent parameters

Solvent	π^*	β	α
Methanol	0.60	0.63	0.98
Ethanol	0.54	0.77	0.86
Propan-2-ol	0.46	0.95	0.78
Butanol	0.46	0.88	0.79
<i>t</i> -Butanol	0.41	1.01	0.62
Ethylene glycol	0.85	0.52	0.92
Dimethyl acetamide	0.88	0.76	–
Methyl acetate	0.60	0.42	–
Ethyl acetate	0.55	0.45	–
Dimethyl sulphoxide	1.00	0.76	–
Dimethyl formamide	0.88	0.69	–
Acetonitrile	0.85	0.31	0.15
Diethyl ether	0.27	0.47	–
Dioxane	0.55	0.37	–
Tetrahydrofuran	0.58	0.55	–

The results of the correlation of the absorption frequencies with the solvent parameters are given in Equations (2), (3) and (4) for the acids in protic solvents (alcohols), and in Equations (5), (6) and (7) for the acids in aprotic solvents.

For benzoic acid in alcohols:

$$\nu = 35.90 - 0.48\pi^* - 0.147\beta + 0.137\alpha \quad (2)$$

$$(r = 0.9844, s = 0.012, n = 6)$$

For cyclohex-1-enylcarboxylic acid in alcohols:

$$\nu = 41.34 + 0.25\pi^* + 2.74\beta + 2.84\alpha \quad (3)$$

$$(r = 0.9520, s = 0.107, n = 6)$$

Finally, for 2-methylcyclohex-1-enylcarboxylic acid in alcohols:

$$\nu = 41.74 + 0.20\pi^* + 2.49\beta + 2.73\alpha \quad (4)$$

$$(r = 0.966, s = 1.023, n = 6)$$

It can be noticed that the π^* parameter (solvation effects) has a different sign for benzoic acid than for the other two acids. A negative sign of the solvatochromic coefficient (s) denotes better solvation in the *transition* state ($n \rightarrow \pi^*$) with a lower dipole moment, while a positive one stands for better solvation in the *ground* state. According to this, benzoic acid is more effectively solvated in the transition state in alcohols, but the other two acids are more effectively solvated in the ground state. The contribution of solvation effects is almost the same for both cyclohexenyl acids and it is not strong, judging by the value of the coefficient related to π^* (s). The β parameter (HBA effects) also favours the ground state, influencing more strongly the non-substituted acid (slightly higher value of β). As the parameter α also has a positive sign, the ground state is favoured by HBD effects, too.

All the described results are opposite to those for benzoic acid, where higher conjugation of the aromatic ring and the carboxyl group exists than in the non-aromatic acids. Only HBD effects stabilize the ground state, however their influence is as small as the influence of the other two effects, signifying that the aromatic acid is not very sensitive to the solvent.

In aprotic solvents (Table III), the wavelengths of the absorption maxima of benzoic acid are almost unchanged in comparison with the results in alcohols, while the other two acids have considerably longer λ_{\max} values.

All this points to the fact that solvent effects have a greater influence on the cyclohexenyl acids than on benzoic acid. The reverse is true in alcohols, the absorption maxima of 2-methylcyclohex-1-enylcarboxylic acid are at longer wavelengths than those of cyclohex-1-enylcarboxylic acid, except for the spectra registered in dioxane and tetrahydrofuran, which indicates that the carbonyl electronic transition is of lower energy in the substituted acid.

TABLE III. Absorption maxima of the acids in aprotic solvents

Solvent	λ_{\max}/nm		
	Benzoic acid	Cyclohex-1-enylcarboxylic acid	2-Methylcyclohex-1-enylcarboxylic acid
Dimethyl acetate	278.8	273.0	–
Methyl acetate	279.2	257.2	259.6
Ethyl acetate	279.2	252.6	254.0
Dimethyl sulphoxide	279.2	261.6	262.4
Dimethyl formamide	278.6	268.2	268.4
Acetonitrile	279.2	252.8	256.0
Diethyl ether	279.6	217.6	218.4
Dioxane	280.2	253.6	252.2
Tetrahydrofuran	279.4	256.0	253.0

For aprotic solvents, where only the solvent polarity (π^*) and HBA effects (β) are present, the following expressions were obtained as a result of the correlation of the absorption maxima with solvent parameters.

Benzoic acid:

$$\nu = 35.66 + 0.135\pi^* + 0.145\beta \quad (5)$$

$(r = 0.9601, s = 0.015, n = 7)$

Cyclohex-1-enylcarboxylic acid:

$$\nu = 42.685 - 18.16\pi^* + 16.825\beta \quad (6)$$

$(r = 0.9713, s = 0.947, n = 6)$

2-Methylcyclohex-1-enylcarboxylic acid:

$$\nu = 42.597 - 17.88\pi^* + 16.44\beta \quad (7)$$

$(r = 0.966, s = 1.023, n = 6)$

Both the examined acids with the cyclohexene ring are better stabilized in their transition state in aprotic solvents. The coefficient related to π^* has a somewhat higher value for the non-substituted acid, meaning that the solvation effects of aprotic solvents on this acid are more expressed than on the methyl-substituted one. This could be explained by the steric effects of the methyl group on the second carbon atom which makes the carboxyl group less approachable for the solvent. The HBA effects stabilize the ground state, again more strongly expressed for the non-substituted acid. However, they work in the opposite direction to the solvation effects, which partly diminishes their influence.

Considering the correlation results for both cyclohexenyl acids together, it can be noticed that the solvation effects are stronger in aprotic solvents, taking the value of the s coefficient as a measure of their intensity. The HBA effects can also be

compared and they are again more intensive in aprotic solvents, which makes this type of solvent convenient for observing the influence of the solvent on the behaviour of these acids in chemical reactions.

The absorption maxima of benzoic acid are in approximately the same range both in alcohols and aprotic solvents. Contrary to this, the other examined acids show considerably lower absorption maximum wavelengths in alcohols than in aprotic solvents, which signifies the $n \rightarrow \pi^*$ transition is of lower energy in the latter type of solvent.

The results obtained in this work are in accordance with our unpublished kinetic data concerning the esterification of cyclohex-1-enylcarboxylic acid and 2-methylcyclohex-1-enylcarboxylic acid with diazodiphenylmethane in a number of protic and aprotic solvents. The same opposing solvent effects on the two examined acids, this time on their reaction rate, was noticed.

EXPERIMENTAL

Materials

The non-substituted cyclohex-1-enylcarboxylic acid b. p. 137 °C, at 15 mmHg (Ref. 9, 137 °C, at 15 mmHg) was synthesized using the Wheeler and Lerner's method,⁸ from cyclohexanone and sodium cyanide. The obtained cyanohydrine was dehydrated to cyanocyclohex-1-ene. The nitrile was hydrolysed with potassium hydroxide to cyclohex-1-enylcarboxylic acid, using hydrochloric acid to adjust the pH.

The same procedure was applied for 2-methylcyclohex-1-enylcarboxylic acid⁸ (m. p. 85–87 °C, at 15 mmHg, Ref.9, 87°C, at 15 mmHg), this time using 2-methylcyclohexanone as the starting ketone.

Benzoic acid was a commercial product (*Fluka*) of p.a. quality.

All the applied chemicals were of p.a. purity.

Spectroscopic measurements

The UV spectra of cyclohex-1-enylcarboxylic acid, 2-methylcyclohex-1-enylcarboxylic acid and benzoic acid in organic solvents of different polarity and structure were recorded using a SHIMADZU UV-160A spectrophotometer. The wavelength range was 200–400 nm. The concentrations of the examined solutions were 10^{-4} mol/dm³. The solvents used were of high purity, designed for spectroscopic measurements.

ИЗВОД

ЕФЕКТИ РАСТВОРАЧА НА ЕЛЕКТРОНСКЕ АПСОРПЦИОНЕ СПЕКТРЕ ЦИКЛОХЕКС-1-ЕНИЛКАРБОНСКЕ И 2-МЕТИЛЦИКЛОХЕКС-1-ЕНИЛКАРБОНСКЕ КИСЕЛИНЕ

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Ултраљубичасти апсорпциони спектри циклохекс-1-енилкарбонске и 2-метилциклохекс-1-енилкарбонске киселине су одређени у шест протичних и девет апротичних растварача у опсегу таласних дужина од 200 до 400 nm. Положај λ_{\max} за испитиване киселине показао је да су апсорпциони максимуми за циклохекс-1-енилкарбонску киселину у протичним растварачима увек на већим таласним дужинама од оних за 2-метил-

циклохекс-1-енилкарбонску киселину. Резултати у апротичним растварачима су показали управо супротно. Да би се објаснили добијени резултати ултраљубичасте апсорпционе фреквенце електронских прелаза у карбонилним групама испитиваних киселина су корелисане тоталном солватохромном једначином облика: $\nu = \nu_0 + s\pi^* + a\alpha + b\beta$ где је π^* мерило поларности растварача, β представља скалу базичности растварача као акцептора протона у водоничној вези, а α представља скалу киселости растварача као донора протона у водоничној вези. Корелације спектроскопских података су изведене помоћу вишеструке линеарне регресионе анализе и разматрани су супротни ефекти растварача на ултраљубичасте апсорпционе максимуме испитиваних киселина.

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