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Spectrochimica Acta Part A 58 (2002) 1437–1442

SPECTROCHIMICA
ACTA
PART A

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Solvent effects on OH stretching frequencies for 1-arylallyl alcohols

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Received 3 March 2001; received in revised form 18 July 2001; accepted 23 July 2001

Abstract

A series of 1-arylallyl alcohols were prepared and its OH stretching frequencies measured in 20 different non-HBD solvents at room temperature. It is noticed that the observed stretching bands were highly sensitive to the nature of the solvents. Multiple parameter equations were applied to investigate the solvent effects on the O–H stretching frequency. The most significant solvent parameters were the nucleophilicity measuring parameter (*B*) and Gutmann donor number (DN), whilst the electrophilicity measuring parameter (*E*) is not significant. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solvent effects; Allyl alcohols; Infrared spectroscopy

1. Introduction

It is generally found that the position, intensity, and shape of absorption bands are usually influenced by solvents of different polarity [1,2].

These modifications are a result of inter-molecular solute–solvent interaction forces, such as ion–dipole, dipole–dipole, dipole-induced dipole, and hydrogen bonding which will tend to alter the energy difference between ground and excited state of the absorbing species containing the chromophore [3].

The O–H stretching vibration of an alcohol in dilute solution is affected by intra- and inter-molecular interactions, the former depends on the molecular structure of the alcohol only, and measurements in the gas phase can give information on this type of interaction [4]. The latter interaction roughly depends on the type of solvent and the molecular structure of the alcohol.

Intra- and inter-molecular hydrogen bonding results in a downward frequency shift and a very considerable broadening and intensification of the O–H absorption band [5,6]. Solvents interact with alcohol molecules through a bulk effect with the molecule as a whole and through local interaction with the hydroxy group. In principle, the local solute–solvent interaction can occur either through association with the hydroxyl H-atom or through the oxygen lone pair [7].

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PII: S1386-1425(01)00591-1

Much attention has been paid to the chemistry of allylic compounds because of their great synthetic utilities, and their widely theoretical studies [8].

In the present work, we investigate the solvent effect on the infrared (IR) stretching frequencies of O–H for a series of 1-arylallyl alcohols (Scheme 1).

Various multiple-parameter equations were applied to explain the solvent effects [9–11].

2. Experimental

2.1. Infrared spectra

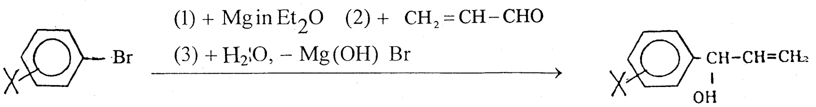
The IR spectra were measured with a Pye-Unicam SP 3-200 and Perkin–Elmer 580B spectrophotometer. Scan time was 10 and 20 min, respectively, using 'liquid' cells with sodium chloride windows, an equivalent cell with the pure solvent was used in the compensating beam. The concentration of the alcohol solutions usually was in the range of 0.04–0.06 M, between these limits the OH stretching frequencies showed no concentration dependence. In general, the frequencies reported are accurate within ± 1 cm^{-1}.

2.2. Solvent purifications

Solvents were purified by standard methods [12], and stored in dark bottles over molecular sieves type 4 Å. *n*-Hexane, cyclohexane, benzene (PhH), bromobenzene (PhBr), chlorobenzene (PhCl), $CHCl_3$, CCl_4, CH_2Cl_2, $ClCH_2CH_2Cl$ and Cl_3CCH_3, were washed with conc. H_2SO_4, 10% $NaHCO_3$, and finally with water, dried, and distilled. Acetone and ethylmethylketone (EMK) were refluxed with $KMnO_4$, then distilled. MeCN, $MeNO_2$, DMF, and DMSO were spectroscopic grade. 1,4-Dioxane was refluxed over sodium until sodium became bright, then distilled. Tetrahydrofuran (THF) was refluxed with $LiAlH_4$, then distilled. Diethylether (DEE) and toluene (PhMe) were dried with sodium then distilled, anisole (PhOMe) was shaked with 2 M NaOH then with water, dried, and distilled over sodium.

2.3. General procedure for preparation of 1-arylallyl alcohols

Substituted bromobenzene (0.1 mol) dissolved in dry diethyl ether, 75 ml in a dropping funnel, few drops of it were added to a suspension of magnesium (0.1 mol) and iodine crystals in dry DEE (75 ml). The reaction mixture was stirred until the iodine color disappeared, then the whole substituted bromobenzene solution was added dropwise, the reaction mixture was boiled until all magnesium reacted. After cooling with ice. Freshly distilled acroleine (0.1 mol) in dry DEE (50 ml) was added dropwise during 2 h, in ice bath, stirring was continued for 12 h. The magnesium salt was then decomposed with an ice-cold saturated aqueous solution of ammonium chloride, the ether layer was washed twice with water and dried with $MgSO_4$, the DEE was evaporated, and the crude product was fractionally distilled under reduced pressure; the middle fraction was redistilled and used in this study.



	X		X
a	H	e	o-OCH_3
b	o-CH_3	f	m-O CH_3
c	m-CH_3	g	p-O CH_3
d	p-CH_3	h	p-Cl

Scheme 1.

Table 1
The O–H stretching frequencies of eight 1-arylallyl alcohols in 20 different solvents

Number	Solvent	$\bar{\nu}$ OH (cm^{-1}) for substituted 1-phenylallyl alcohols							
		Sub. =H	*p*-MeO	*m*-MeO	*p*-Me	*m*-Me	*p*-Cl	*o*-MeO[a]	*o*-Me
1	*n*-Hexane	3621	3620	3624	3621	3624	3625	3628	3626
2	Cyclohexane	3624	3617	3621	3619	3620	3624	3628	3622
3	$CC1_4$	3615	3614	3620	3617	3612	3616	3621	3621
4	$CHC1_3$	3595	3592	3595	3594	3590	3590	3605	3601
5	CH_2Cl_2	3583	3593	3586	3587	3587	3585	3601	3590
6	$(CH_2Cl)_2$	3584	3576	3580	3580	3578	3582	3602	3585
7	$C1_3CCH_3$	3604	3605	3603	3597	3597	3605	3601	3605
8	PhH	3574	3577	3582	3578	3575	3575	3583	3575
9	PhMe	3582	3576	3575	3578	3577	3572	3586	3578
10	PhCl	3590	3585	3583	3587	3584	3585	3584	3580
11	PhOMe	3526	3507	3512	3508	3497	3500	3507	3495
12	1,4-Dioxane	3457	3453	3422	3440	3410	3410	3469	3426
13	DEE	3453	3445	3432	3455	3430	3425	3469	3460
14	THF	3439	3442	3424	3408	3433	3424	3442	3390
15	MeCN	3511	3517	3492	3487	3492	3470	3496	3490
16	$MeNO_2$	3555	3550	3541	3545	3548	3535	3567	3552
17	Acetone	3224	3425	3410	3425	3535	3432	3514	3464
18	EMK	3460	3485	3482	3475	3495	3480	3531	3475
19	DMF	3343	3345	3318	3352	3335	3260	3310	3300
20	DMSO	3295	3245	3248	3295	3280	3215	3277	3270

$\varepsilon = 45–140$ mol^{-1} l cm^{-1}; $\nu_{1/2} = 0.2–0.3$ cm^{-1} for solvents number 1–10 while $\varepsilon = 120–360$ mol^{-1} l cm^{-1}; $\nu_{1/2} = 0.8–6$ cm^{-1} for solvents number 11–20.

[a] The second absorption band appears in solvents (1–7) at 3584, 3592, 3561, 3565, 3565, 3554, and 3560 cm^{-1}, respectively.

3. Results and discussion

The O–H stretching frequencies of eight 1-arylallyl alcohols (Scheme 1) measured at room temperature in 20 different solvents are listed in Table 1.

In general, as the solvent polarity increases the observed absorption band becomes broader and more intense, this can be attributed to the increasing polarity of O–H bond, which might, therefore, be expected to show a greater difference between the O–H bond dipole moment in the ground and excited state.

The observed shapes of the O–H stretching were symmetric, asymmetric, with a shoulder or well splitted (Fig. 1). These effects can be explained either on the basis of intra- and intermolecular hydrogen bonding, the presence of a second band caused by Fermi-resonance with the combination band of the α-CH group, or the oxygen lone pair interaction with a hydrogen atom and the rotation of the OH group around C–O axis which can be either free or partially hindered, accordingly leading to a few energetically favorable conformations.

The calculated heats of formation (ΔH_f) for the different conformations of 1-phenylallyl alcohol, using MINDO-forces program 13, are shown in Scheme 2.

MINDO-forces approximation based on MINDO/2 approximation using MINDO/3 parameters for core repulsion functions, and energy was minimized as a function of geometry using Pulay's force method [13].

It can be seen from the calculated heats of formation that the rotational barrier is easily overcome at room temperature. Hence, alcohols in solution can be present in many different conformations.

It can be seen from Table 1 that $\bar{\nu}$ values for the alcohols in the same solvent are almost constant. This can be explained by either the skeleton is always present in the same favorable conformation or that the different orientations about the C–C axis have no effect on the OH stretching frequency.

On the other hand, plotting the OH stretching frequency of one of the phenylallyl alcohols against the OH stretching frequency of other substituted phenylallyl alcohols in different solvents gives a good linear correlation ($0.97 \leqslant r \leqslant 0.99$), indicating that the solvents interact with the OH groups of all arylallyl alcohols by the same interaction mechanism.

1-(*o*-Methoxyphenyl) allyl alcohol shows two peak maxima in the O–H stretching region in solvents number 1–7 (Table 1; Fig. 1). This observation is due to presence of at least two conformers, freely and intra-molecular hydrogen-bonded.

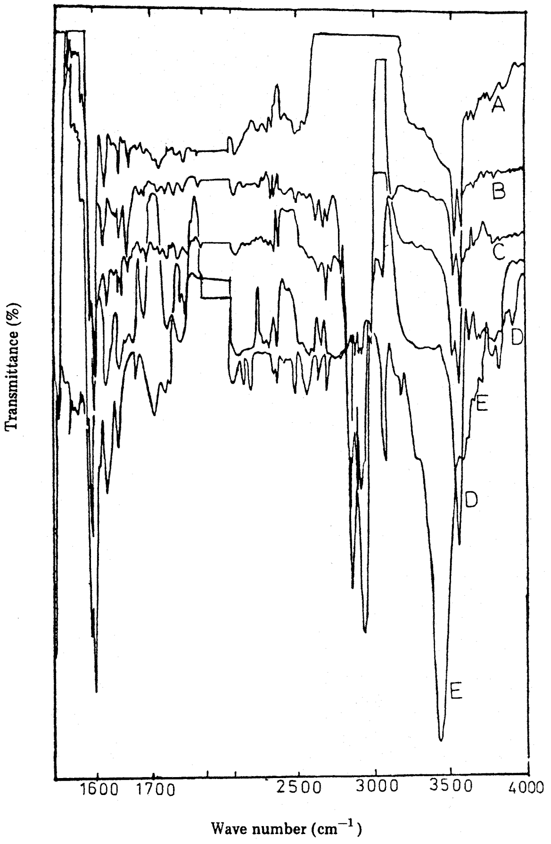
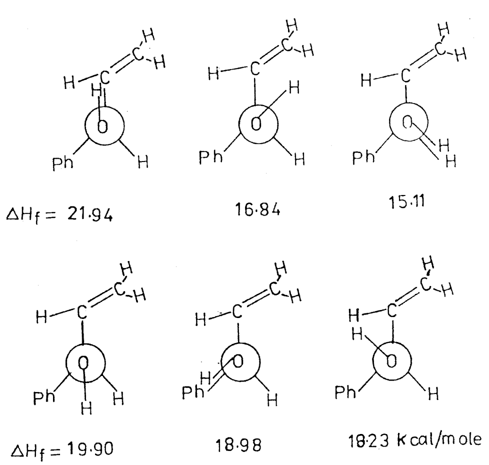
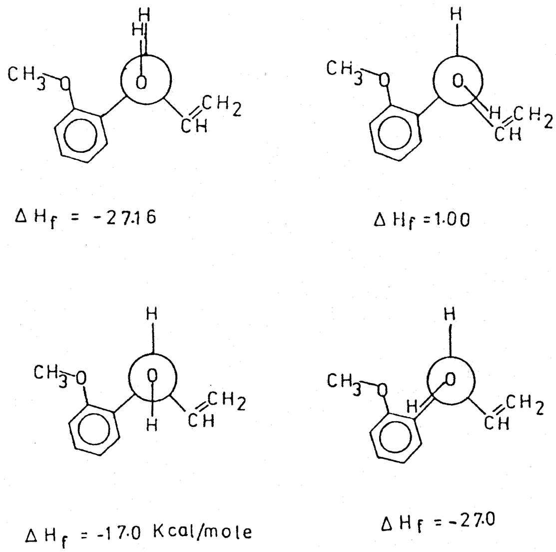


Fig. 1. Part of the IR spectrum of 1-(-*o*-methoxyphenyl) allyl alcohol in (A) *n*-hexane, (B) CCl_4, (C) $CHCl_3$, (D) PhH, and (E) 1,4-dioxane.



Scheme 2. Newman projection along the C–O bond of 1-phenylallyl alcohols showing different rotamers and their heats of formation.



Scheme 3. Newman projection along the C–O of 1-(*o*-methoxyphenyl) allyl alcohol showing different rotamers and its heats of formation.

The calculated heats of formation for different conformations of 1-(*o*-methoxyphenyl) allyl alcohol are shown in Scheme 3, which clearly indicates the presence of two conformers. In non-polar aromatic solvents, such as PhH and PhMe, only one absorption maximum is observed. This indicates that the free conformers were associated with the π-electrons of the aromatic solvents forming (π···HO) inter-molecular hydrogen bonding, which appears in the same region of (O···HO) hydrogen bonds.

The IR-spectroscopic data of Table 1 were treated statistically in terms of generalized multiple parameter correlation equations, which split the gross solvent effects into separate independent contributions corresponding to different type of solvent–solute interaction mechanism. Tables 2–4 represent Koppel–Palm, Taft–Kamlet, and Krygowski–Fawcett equations [9–11], analysis results from multiple regression of OH stretching frequencies.

The sequence of importance of solvent parameters during the stepwise regression analysis were firstly the basicity measuring parameters B, β, and donor number (DN), then the dipolarity-polarizability measuring parameters Y, P, π^* and E_T, and finally the acidity measuring parameter E and α. The sequence of solvent parameters indicates that major effecting parameters were the basicity measuring parameters and the minor effecting parameters the acidity measuring parameters.

The negative sign of B, β, DN, π^*, Y, and E_T coefficients indicate the inverse proportionality of these parameters with O–H stretching frequencies (Tables 2–4). This means that, as the basicity of the solvent increases the O–H stretching frequency decreases, due to formation of a stronger hydrogen bond between the solvent and the O–H hydrogen atom. On the other hand, as the polar-

Table 2
Correlation analysis of $\bar{\nu}$ OH for substituted 1-arylallyl alcohols using the Koppel–Palm equation [9]

Subst.	$\bar{\nu} = C+eE+bB+yY=pP^{a}$					R
	C	E	B	y	p	
H	3698.7 ± 35.0	0.003 ± 2.6	−1.80 ± 0.1	−63.73 ± 50.2	−39.42 ± 138.9	0.97
p-MeO	3739.4 ± 44.1	−1.24 ± 3.2	−1.92 ± 0.12	−38.9 ± 63.2	−273.1 ± 174.9	0.95
m-MeO	3718.7 ± 37.8	−2.41 ± 2.8	−2.04 ± 0.11	−32.13 ± 54.2	−122.27 ± 149.9	0.97
p-Me	3709.3 ± 25.5	−085 ± 1.82	−1.83 ± 0.07	−54.1 ± 35.2	−109.3 ± 97.4	0.98
m-Me	3718.9 ± 31.1	−3.04 ± 2.3	−1.94 ± 0.09	+11.78 ± 44.6	−220.5 ± 1 23.4	0.98
p-Cl	3750.3 ± 50.1	−4.89 ± 3.7	−2.2 ± 0.14	−20.4 ± 71.9	−241.7 ± 199.0	0.96
o-MeO	3778.4 ± 55.3	−1.85 ± 4.1	−1.9 ± 0.16	−24.8 ± 79.3	−399.4 ± 219.4	0.93
o-Me	3754.7 ± 35.9	−1.28 ± 2.6	−2.05 ± 0.1	−27.3 ± 51.5	−296.4 ± 142.4	0.97

[a] $\bar{\nu}$and C represent the parameters A and A_0 in the original equation, the E and B terms represent the solvents electrophilicity and nucleophilicity. The Y and P terms represent functions of the solvents dielectric and polarizability respectively.

Table 3
Correlation analysis of $\bar{\nu}$ OH for substituted 1-arylallyl alcohols using the Kamlet–Taft equation [11]

Subst.	$\bar{\nu} = C+s(\pi^*-0.38\delta)+b\beta+a\alpha^{a}$				r
	C	s	b	A	
H	3621.91 ± 6.96	−64.57 ± 23.24	−311.4 ± 25.9	75.4 ± 44.0	0.97
p-MeO	3621.99 ± 11.2	−79.14 ± 37.4	−308.8 ± 41.8	117.5 ± 70.9	0.94
m-MeO	3624.3 ± 10.5	−79.5 ± 35.0	−336.7 ± .2	96.9 ± 66.4	0.95
p-Me	3618.4 ± 7.2	−66.4 ± 24.1	−311.1 ± 26.9	74.3 ± 45.6	0.97
m-Me	3615.9 ± 11.5	−68.3 ± 38.4	−313.2 ± 42.9	95.2 ± 72.7	0.94
p-Cl	3628.5 ± 13.6	−94.1 ± 35.5	−357.9 ± 50.8	108.0 ± 86.2	0.94
o-MeO	3630.2 ± 15.2	−79.9 ± 50.8	−291.2 ± 56.8	124.8 ± 96.3	0.89
o-Me	3624.4 ± 10.5	−84.4 ± 35.0	−324.5 ± 39.1	126.3 ± 66.4	0.95

[a] $\bar{\nu}$ and C represent the parameter XYZ and XYZ_0 in the original equation, π^* a scale of the solvents dipolarity-polarizability, α and β represent a scale of the solvents hydrogen bonding donor and acceptor capability, respectively.

Table 4
Correlation analysis of $\bar{\nu}$ OH for substituted 1-arylallyl alcohols using the Krygowski–Fawcett equation [10]

Subst.	$\bar{\nu}=C+\alpha E_T+\beta DN^a$			r
	C	α	β	
H	3692.5 ± 42.3	-2.90 ± 1.10	-1.84 ± 0.11	0.96
p-MeO	3679.1 ± 51.4	-2.49 ± 1.30	-1.96 ± 0.11	0.94
m-MeO	3706.3 ± 42.5	-3.31 ± 1.13	-2.06 ± 0.12	0.97
p-Me	3696.8 ± 29.8	-3.09 ± 0.79	-1.85 ± 0.08	0.96
m-Me	3672.8 ± 42.0	-2.45 ± 1.12	-1.94 ± 0.11	0.95
p-Cl	3728.5 ± 56.2	-3.94 ± 1.50	-2.20 ± 2.20	0.95
o-MeO	3696.4 ± 62.3	-2.66 ± 1.66	-1.89 ± 0.17	0.92
o-Me	3690.3 ± 44.2	-2.80 ± 1.13	-2.06 ± 0.13	0.96

[a] $\bar{\nu}$ and C represent Q and Q_0 in the original equation, E_T and DN represent the solvents Dimroth–Reichardt constant and the DN, respectively.

ity of the solvent increases the O–H stretching frequency decreases, this is due to a stronger polarization of O–H bond which leads to a decrease of the OH bond force constant.

The positive sign of the hydrogen bonding donor parameter (α) coefficients indicates its direct proportionality to the O–H stretching frequency, which means that, as the acidity of the solvent increases, the stronger interaction with the oxygen lone pair of the hydroxyl group leads to an increase in the O–H stretching frequency.

The electrophilicity measuring parameter (E) is a non-significant parameter because its coefficient value is lower than its standard error Table 2.

4. Summary

Twenty non-HBD solvents effect on the O–H stretching frequency of eight phenyl substituted 1-phenylallyl alchohols were performed. The quantitative description of the solvent effects by mean of correlation analysis with three well-known multiparameter equations were carried out. The three applied multiparameter equation describe the solvent effects approximately to equal extent.

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