Solvent Effects on OH Stretching Frequencies for 3-Arylallyl Alcohols

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Eight 3-arylallyl alcohols were prepared, and their OH stretching frequencies were measured in twenty non-HBD solvents at room temperature. The observed stretching bands were highly sensitive to the nature of the solvents. Multiple parameter equations were applied to investigate the solvent effect on the O–H stretching frequency. The most significant solvent parameters were the nucleophilicity parameter and the Gutmann donor number, while the electrophilicity parameter was not significant.

Key words: Solvent Effects; Allyl Alcohols; IR-Spectroscopy.

Introduction

Allylic compounds are those organic compounds having an ethylenic linkage to a carbon, bearing either an electronegative functional group such as Cl, Br, OH, or OR, or an electropositive group such as RMgX, Li, Na or K. The ethylenic bond of the allylic system activates the functional group [1].

Much attention has been paid to the chemistry of allylic compounds because of their utility [2].

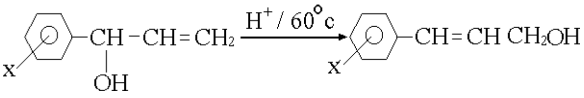
It is found that the position, intensity, and shape of the absorption bands are influenced by solvents of different polarity [3, 4].

These modifications result from intermolecular solute/solvent interactions such as ion-dipole, dipole-dipole, dipole-induced dipole, and hydrogen bonding, which tend to alter the energy difference between the ground and excited state of the absorbing species containing the chromophore [5].

The O–H stretching vibration of an alcohol in dilute solution is affected by intra- and intermolecular interactions, the former depending on the molecular structure of the alcohol only; measurements in the gas phase can give information on this type of interaction [6]. The latter interaction depends also on the type of solvent [7].

Solvents interact with alcohol molecules through an effect with the molecule as a whole and through a 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 [8].

In the present work we have investigated the effect of twenty solvents on the O–H IR stretching frequencies of eight 3-arylallyl alcohols:



	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.

Various equations of the general form were applied to explain the solvent effects [9 – 11].

$$A = A_o + bB + cC + dD + \ldots . \qquad (1)$$

A is a solvent dependent physico-chemical property. A_o corresponds to this property in the gas phase or in an inert solvent; $B, C, D, \ldots$ represent independent but complementary solvent parameters which account for the different solute/solvent interaction mechanisms; $b, c, d, \ldots$ are the coefficients describing the sensitivity of the property A to the different solvent/solut interaction mechanisms [3].

Table 1. The O–H stretching frequencies of eight 3-arylallyl alcohols in twenty different solvents*.

No.	Solvent	$\bar{\nu}$ OH (cm^{-1}) for substituted 3-phenylallyl alcohols							
		sub.=H	p–MeO	m–MeO	p–Me	m–Me	p–Cl	o–Meo	o–Me
1	n-hexane	3623	3625	3625	3622	3625	3627	3632	3629
2	cyclohexane	3623	3621	3622	3621	3621	3628	3630	3630
3	CCl_4	3618	3615	3621	3621	3618	3617	3625	3624
4	$CHCl_3$	3598	3603	3600	3601	3600	3602	3600	3605
5	CH_2Cl_2	3597	3602	3596	3598	3595	3595	3601	3605
6	$(CH_2Cl)_2$	3591	3592	3588	3585	3585	3590	3592	3597
7	Cl_3CCH3	3605	3598	3600	3598	3600	3597	3601	3602
8	PhH	3578	3578	3587	3585	3583	3586	3580	3587
9	PhMe	3585	3578	3583	3583	3585	3592	3587	3583
10	PhCl	3592	3590	3595	3590	3594	3592	3588	3589
11	PhOMe	3580	3540	3515	3510	3525	3523	3550	3518
12	1,4-Dioxane	3460	3475	3880	3462	3467	3460	3487	3446
13	DEE	3435	3486	3495	3477	3465	3445	3460	3465
14	THF	3460	3490	3460	3452	3451	3460	3430	3428
15	MeCN	3470	3480	3512	3515	3510	3500	3510	3520
16	$MeNO_2$	3485	3560	3557	3555	3557	3558	3540	3552
17	Acetone	3486	3470	3465	3445	3565	3455	3485	3470
18	EMK	3480	3510	3470	3477	3515	3510	3495	3495
19	DMF	3350	3390	3365	3360	3285	3350	3325	3318
20	DMSO	3296	3285	3255	3290	3275	3300	3285	3270

* $\varepsilon = 35 - 150$ $mole^{-1}$ l cm^{-1}; $\nu_{1/2} = 0.3 - 0.35$ cm^{-1} for solvents number $1 - 10$ while $\varepsilon = 150 - 360$ $mole^{-1}$ l cm^{-1}; $\nu_{1/2} = 0.6 - 6$ cm^{-1} for solvents number 11 – 20.

Experimental

Infrared spectra: The infrared spectra were measured with a Pye-Unicam SP 3-200 and Perkin-Elmer 580B spectrophotometer. The scan time was 10 and 20 minutes, respectively, using "liquid" cells with sodium chloride windows. An equivalent cell with the pure solvent in the same beam was used. The concentration of the alcohol solutions 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}.

Solvent purifications: Solvents were purified by standard methods [12] and stored in dark bottles over molecular sieves type 4 A°.

n-hexane, cyclohexane, benzene (PhH), bromobenzene (PhBr), chlorobenzene (PhCl), $CHCl_3$, CCl_4, CH_2Cl_2,CH_2ClCH_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 $KMnO_4$ and then distilled. MeCN, $MeNO_2$, DMF, and DMSO were of spectroscopic grade. 1,4-Dioxane was refluxed over sodium until sodium became bright, and then distilled. Tetrahydrofuran (THF) was refluxed with $LiAlH_4$, and then distilled. Diethylether (DEE) and toluene (PhMe) were dried with sodium, and then distilled, anisole (PhOMe) was shaked with 2M NaOH then with water, dried, and distilled over sodium.

For the preparation of the 3-arylallyl alcohols, a solution of substituted 1-phenylallyl alcohol (5 g) in 60% aqueous acetone (150 ml), acidified with HCl, was refluxed in a water bath for 5 hrs. Then the acetone was distilled off and the aqueous solution, neutralized with 20% sodium carbonate, was extracted with ether (2 × 50 ml). The ether layer was washed twice with water and dried with $MgSO_4$. The diethylether was evaporated and the crude product was either fractionally distilled under reduced pressure, the middle fraction being redistilled and used in this study, or crystalized from benzene-petroleum ether in case of solid compounds [13].

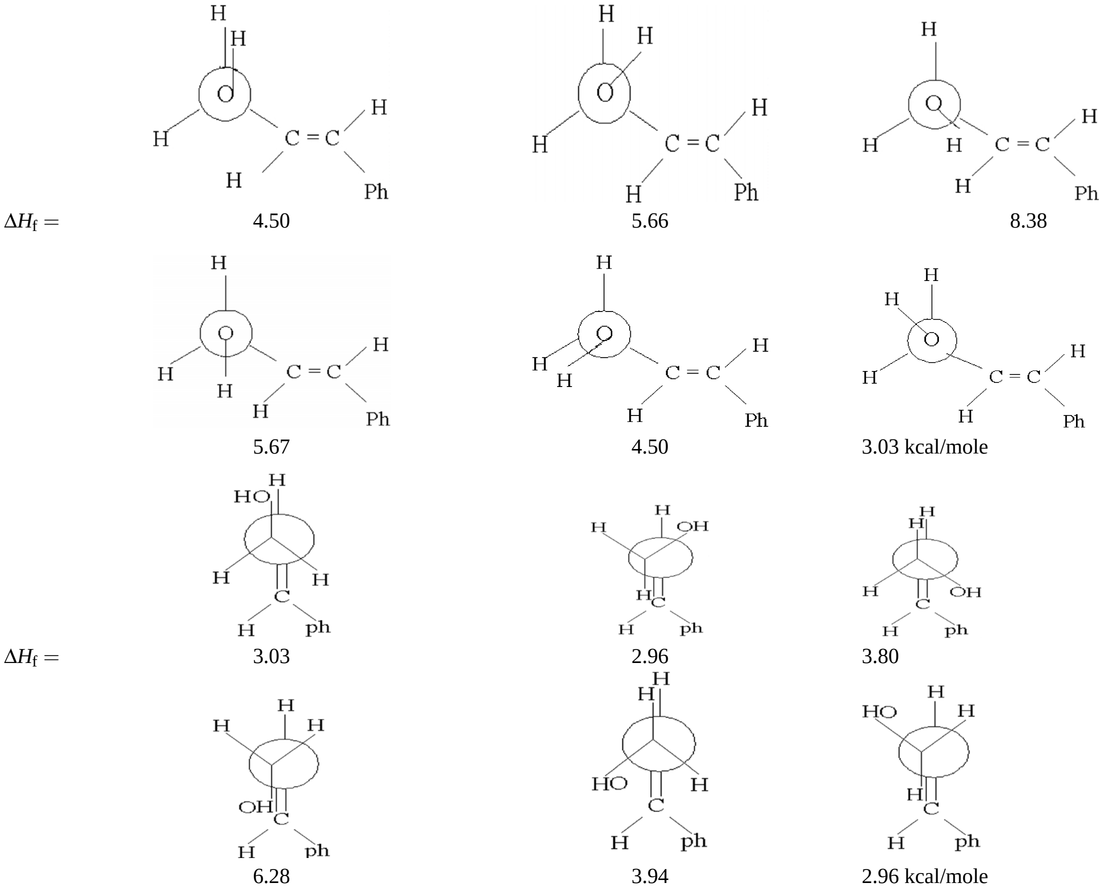
Results and Discussion

The O–H stretching frequencies of the eight 3-arylallyl alcohols, see Scheme 1, measured at room temperature in twenty 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 the O–H bond, which might, therefore, 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 or asymmetric with a shoulder band. These effects can be explained on the basis of intra- and intermolecular hydrogen bonding.

The calculated heats of formation (ΔH_f) of the different conformations of 3-phenylallyl alcohol, using the MINDO-forces program [14], are shown in



Scheme 2. Newman projection along the C–O and C-C bond of 3-phenylallyl alcohols, showing different rotamers and their heats of formation.

Scheme 2, whereby the molecular energy, obtained from semi empirical MINDO/3 MO, was completely minimized by the Mutargh-Sargent technique. The derivative of the energy was calculated according to Pulay's force method. The program allows the variation of the β-parameter with a geometrical change in a consistent way. A full description of the program and it's application is given in [14].

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 the $\bar{\nu}$ values for the alcohols in the same solvent are almost constant. Thus either the skeleton is always present in the same favorable conformation, or 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 a phenylallyl alcohol against that of another substituted phenylallyl alcohol in different solvents gives a good linear correlation ($0.97 \le r \le 0.99$), indicating that the solvents interact with the OH groups of all arylallyl alcohols by the same interaction mechanism.

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 types of solvent-solute interaction mechanisms. Tables 2, 3, and 4 represent the results of the analysis by the Koppel-Palm, Taft-Kamlet, and Krygowski-Fawcett equations [9 – 11].

The solvent parameters during the stepwise regression analysis were firstly the basicity measuring parameters *B*, β, and the donor number *DN*, then the

Subst.	$\bar{\nu} = C + eE + bB + yY + pP$ *					r
	C	e	B	y	p	
H	3677.4 ± 11.1	-8.3 ± 3.14	-1.70 ± 0.12	***	***	0.94
p–MeO	3758.8 ± 64.5	-5.0 ± 2.87	-1.65 ± 0.11	***	-401.3 ± 299.7	0.94
m–MeO	3844.6 ± 75.1	***	-1.77 ± 0.13	-108.0 ± 61.8	-649.8 ± 327.3	0.94
p–Me	3776.6 ± 57.6	***	-1.75 ± 0.10	-72.69 ± 47.7	-396.2 ± 250.2	0.97
m–Me	3783.4 ± 84.8	***	-1.97 ± 0.14	***	-479.7 ± 396.6	0.92
p–Cl	3676.1 ± 8.17	***	-1.81 ± 0.14	***	***	0.96
o–MeO	3794.1 ± 70.1	***	-1.80 ± 0.12	-102.0 ± 57.7	-396.8 ± 305.5	0.95
o–Me	3801.3 ± 58.9	***	-2.03 ± 0.11	***	-540.9 ± 275.7	0.96

Table 2. Correlation analysis of $\bar{\nu}$ OH for substituted 3-arylallyl alcohols, using the Koppel-Palm equation [9].

* $\bar{\nu}$ 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. *** Not significant parameter, excluded from the regression analysis.

Subst.	$\bar{\nu} = C + s(\pi^* - 0.38\delta) + b\beta + a\alpha$ *				r
	C	s	b	a	
H	3629.91 ± 11.2	-62.8 ± 37.3	-307.8 ± 41.7	-9.39 ± 70.7	0.93
p–MeO	3627.1 ± 11.9	-80.4 ± 39.7	-253.0 ± 44.4	94.5 ± 75.2	0.91
m–MeO	3632.8 ± 10.8	-99.3 ± 36.1	-270.2 ± 40.4	125.3 ± 68.5	0.94
p–Me	3625.2 ± 8.0	-81.8 ± 26.9	-279.2 ± 30.1	114.7 ± 51.0	0.97
m–Me	3631.3 ± 13.3	-93.4 ± 44.5	-293.1 ± 49.7	134.0 ± 84.3	0.94
p–Cl	3625.3 ± 10.2	-65.0 ± 34.1	-295.1 ± 38.1	82.0 ± 64.6	0.94
o–MeO	3633.8 ± 9.8	-79.0 ± 32.6	-300.7 ± 36.4	86.3 ± 61.8	0.95
o–Me	3631.8 ± 10.6	-83.1 ± 35.3	-311.0 ± 39.7	128.3 ± 67.3	0.95

Table 3. Correlation analysis of $\bar{\nu}$ OH for substituted 3-arylallyl alcohols, using the Kamlet-Taft equation [10].

* $\bar{\nu}$ 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 accepter capability, respectively.

Table 4. Correlation analysis of $\bar{\nu}$ OH for substituted 3-arylallyl alcohols, using the Krygowski-Fawcett equation [11].

Subst.	$\bar{\nu} = C + \alpha E_T + \beta DN$ *			r
	C	α	β	
H	3760.5 ± 46.5	-4.78 ± 1.20	-1.67 ± 0.13	0.95
p–MeO	3719.1 ± 46.0	-3.44 ± 1.23	-1.62 ± 0.11	0.94
m–MeO	3737.2 ± 49.0	-3.88 ± 1.31	-1.77 ± 0.12	0.95
p–Me	3707.6 ± 36.6	-3.17 ± 0.98	-1.77 ± 0.10	0.97
m–Me	3713.9 ± 61.0	-3.27 ± 1.60	-1.91 ± 0.17	0.92
p–Cl	3698.5 ± 39.9	-2.86 ± 1.00	-1.80 ± 0.11	0.96
o–MeO	3726.0 ± 48.5	-3.57 ± 1.30	-1.83 ± 0.14	0.95
o–Me	3695.3 ± 48.0	-2.68 ± 1.28	-1.99 ± 0.13	0.95

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

dipolarity-polarizability measuring parameters Y, P, π^*, and E_T, and finally the acidity measuring parameters E and α.

The negative sign of B, β, DN, π^*, Y, and E_T indicates the inverse proportionality of these parameters to the O–H stretching frequencies (Table 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 polarity of the solvent increases the O–H stretching frequency decreases. This is due to a stronger polarization of the 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 it's direct proporationality 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 it's coefficient is lower than it's standard error.

Summary

The effect of twenty non-HBD solvents on the O–H stretching frequency of eight substituted 3-phenylallyl alcohols was studied. The rotational barrier for the OH group can easily be overcome at room temperature. The solvent effects were described by means of correlation analysis with three well-known multiparameter equations describing the effects approximately equally well.

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