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:

\[ \text{X} \quad \text{CH} - \text{CH} = \text{CH}_2 \quad \text{H}^+ / 60^\circ \text{C} \quad \text{X} \quad \text{CH}_2 \text{OH} \]

Scheme 1.

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

\[ A = A_o + bB + cC + dD + \ldots \]  

(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/solute interaction mechanisms [3].
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 Å.

n-hexane, cyclohexane, benzene (PhH), bromobenzene (PhBr), chlorobenzene (PhCl), CHCl₃, CCl₄, CH₂Cl₂, CH₂ClCH₂Cl and C₃Cl₃CH₃, were washed with conc. H₂SO₄, 10% NaHCO₃, and finally with water, dried, and distilled. Acetone and ethylmethylketone (EMK) were refluxed with KMnO₄ and then distilled. MeCN, MeNO₂, DMF, and DMSO were of spectroscopic grade. 1,4-Dioxane was refluxed for sodium until sodium became bright, and then distilled. Tetrahydrofuran (THF) was refluxed with LiAlH₄, and then distilled. Diethylether (DEE) and toluene (PhMe) were dried with sodium, and then distilled, anisole (PhOMe) was shaken 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 MgSO₄. 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 crystallized 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 (ΔHf) of the different conformations of 3-phenylallyl alcohol, using the MINDO-forces program [14], are shown in

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent</th>
<th>ν OH (cm⁻¹) for substituted 3-phenylallyl alcohols</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-hexane</td>
<td>3623 3625 3625 3622 3621 3621 3618 3617 3625 3624</td>
</tr>
<tr>
<td>2</td>
<td>cyclohexane</td>
<td>3623 3621 3622 3621 3621 3628 3630 3630</td>
</tr>
<tr>
<td>3</td>
<td>CCl₄</td>
<td>3618 3615 3621 3621 3618 3617 3625 3624</td>
</tr>
<tr>
<td>4</td>
<td>CHCl₃</td>
<td>3598 3596 3598 3595 3595 3594 3592 3597</td>
</tr>
<tr>
<td>5</td>
<td>CH₂Cl₂</td>
<td>3597 3596 3598 3595 3595 3594 3592 3597</td>
</tr>
<tr>
<td>6</td>
<td>C₃Cl₃CH₃</td>
<td>3605 3598 3596 3595 3595 3594 3592 3597</td>
</tr>
<tr>
<td>7</td>
<td>PhH</td>
<td>3578 3578 3587 3585 3583 3586 3580 3587</td>
</tr>
<tr>
<td>8</td>
<td>PhMe</td>
<td>3585 3578 3583 3583 3585 3585 3582 3585</td>
</tr>
<tr>
<td>9</td>
<td>PhCl</td>
<td>3592 3590 3595 3590 3594 3592 3588 3589</td>
</tr>
<tr>
<td>10</td>
<td>PhOMe</td>
<td>3580 3540 3515 3510 3525 3523 3550 3518</td>
</tr>
<tr>
<td>11</td>
<td>1,4-Dioxane</td>
<td>3460 3475 3880 3462 3467 3460 3487 3446</td>
</tr>
<tr>
<td>12</td>
<td>DEE</td>
<td>3435 3486 3495 3477 3465 3445 3460 3465</td>
</tr>
<tr>
<td>13</td>
<td>THF</td>
<td>3460 3490 3460 3452 3451 3460 3430 3428</td>
</tr>
<tr>
<td>14</td>
<td>MeCN</td>
<td>3470 3480 3512 3515 3510 3500 3510 3520</td>
</tr>
<tr>
<td>15</td>
<td>MeNO₂</td>
<td>3485 3560 3557 3555 3557 3558 3540 3552</td>
</tr>
<tr>
<td>16</td>
<td>acetone</td>
<td>3486 3470 3465 3445 3565 3455 3485 3470</td>
</tr>
<tr>
<td>17</td>
<td>Acetone</td>
<td>3480 3510 3470 3477 3475 3510 3495 3495</td>
</tr>
<tr>
<td>18</td>
<td>EMK</td>
<td>3350 3390 3365 3360 3285 3350 3325 3318</td>
</tr>
<tr>
<td>19</td>
<td>DMF</td>
<td>3296 3285 3255 3290 3275 3300 3285 3270</td>
</tr>
</tbody>
</table>

* ε = 35 – 150 mole⁻¹ cm⁻¹; ν₁/₂ = 0.3 – 0.35 cm⁻¹ for solvents number 1 – 10 while ε = 150 – 360 mole⁻¹ cm⁻¹; ν₁/₂ = 0.6 – 6 cm⁻¹ for solvents number 11 – 20.
Δ\( \Delta H_f \) = 4.50, 5.66, 8.38 kcal/mole

Δ\( \Delta H_f \) = 3.03, 2.96, 3.80 kcal/mole

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 MNDO/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 \( \beta \)-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 ≤ \( r \) ≤ 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 \( B \), \( \beta \), and the donor number \( DN \), then the
allyl alcohols, using the Krygowski-Fawcett equation [11].

\[ \pi = \bar{\nu} \]

The negative sign of \( \bar{\nu} \), \( E \), and \( \nu \) 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 \( O-H \) bond force constant.

The positive sign of the hydrogen bonding donor parameter \( \alpha \) coefficients indicates it’s 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 is lower than its 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.