GAS–SOLVENT SHIFTS FOR THE ν_{OH} FREQUENCY IN SATURATED ALCOHOLS

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ABSTRACT

The transferability of gas–solvent shifts for the ν_{OH} frequencies in several saturated cyclic and acyclic alcohols is examined. Shift averages are established for different kinds of OH rotamers. The established quantities can be employed for the accurate evaluation of ν_{OH} frequencies CCl_4 and CS_2 solutions from the corresponding gas values and vice versa.

INTRODUCTION

In previous papers we have reported on the ν_{OH} gas phase frequency for several types of OH rotamers in saturated alcohols [1–3]. At present we are able to predict these quantities with reasonable reliability by means of a Molecular Mechanics model, using Allinger's MM2 force field extended with monopole interactions between CNDO/2 charges. For practical purposes, however, we are interested in predicting the ν_{OH} frequency of rotamers in apolar solvents, since most studies on the OH stretching band make use of these media. In these solutions the frequency of ν_{OH} appears to be shifted towards lower values with respect to that for the gas phase, due to the interactions between the OH group and solvent molecules. Direct calculation of ν_{OH} in solutions within the Molecular Mechanics framework is not possible at present, as neither empirical parameters nor interaction potentials are available to describe properly the effect of solvation on this frequency.

An alternative approach to obtain solution values, could be one in which the calculated ν_{OH} gas frequency for a given OH rotamer is diminished by the corresponding ν_{OH} gas–solvent shift, $\nu_{\text{OH}}(\text{gas}) - \nu_{\text{OH}}(\text{solvent})$, for the solvent in question. The applicability of this approach, however, requires that these shifts are characteristic for the different OH environments. In this respect, ν_{OH} solvent–solvent shifts have been employed earlier in studying the conformational behaviour of tertiary alcohols by Visser and van der Maas [4]. They have shown that the ν_{OH} frequency difference between the values measured in CCl_4 and CS_2 solutions, $\nu_{\text{diff}}(\text{CCl}_4\text{--CS}_2)$, can be related to the degree of accessibility of the hydroxyl group by solvent molecules. The magnitude

of the ν_{diff} shift appears characteristic for different OH proton environments. In view of this we expect the corresponding ν_{OH} gas-solvent shifts to be characteristic for different OH environments also, since both parameters are correlated. In the following we will examine the extent to which the latter shifts within various kinds of OH rotamers in saturated alcohols are transferable, and illustrate their usefulness for practical applications.

We have selected a number of saturated cyclic and acyclic alcohols for which the rotamer frequencies in gas and in solution of CCl_4 and CS_2 are well established. The different rotamers are grouped in classes according to their OH proton environment, and subsequently the corresponding magnitudes for the shifts are established from the experimental frequencies. The present study is confined to rotamers for which the OH proton environment is determined by the presence of methyl or methylene groups attached to the α - and/or β -carbons.

RESULTS AND DISCUSSION

The data of interest have been collected in Table 1. The nomenclature employed to distinguish different rotamers of the same molecule is as follows: (i) in acyclic compounds the rotamers are denoted *trans* when the OH proton lies between two identical α -substituents and *gauche* when the substituents differ; (ii) in cyclohexanols the rotamers are denoted *A* or *B* according to Fig. 1(a). The subscripts *q* and *x* refer to the conformation (*equatorial* or *axial*).

The classes A, B, C, D, E and F indicate the rotamers with identical atoms in the immediate vicinity of the OH proton as depicted in Fig. 1(b). This classification corresponds to that of Joris et al. [5] except that for practical reasons classes D and F have been interchanged (*vide infra*).

Rotamer gas frequencies have been taken from earlier reported work except for the compounds XV and XVI. We therefore comment briefly how the assignments of the experimental frequencies to the rotamers of these two alcohols have been accomplished. For the former compound the assignment is readily carried out by comparison with the frequencies for the rotamers in compound XII (note that the OH environment of A_q in XV is equivalent to that of A_x in XII, because of the axially positioned β -methyl groups). For the latter compound, since in CCl_4 solution both rotamers are present [6] and only a narrow OH band for the gas phase is observed, the ν_{OH} frequencies of both forms must coincide and the same value is therefore assigned.

In Table 2, the data have been grouped according to the classes to which the rotamers belong. The number of rotamers in each of these classes is given in parentheses. Comparison between the data quoted for the ν_{OH} frequency and for the gas-solvent shifts shows that these two parameters are not correlated, since a given shift interval is not connected with specific values for the frequency.

It appears that the shifts are rather constant within each (sub)class and in general differ significantly from one (sub)class to another. Consequently in

TABLE 1

Experimental ν_{OH} frequencies for saturated alcohols^a

Compound		Rotamer class	ν_{OH} (cm ⁻¹)		
			Gas	CCl ₄ (soln.)	CS ₂ (soln.)
I	Methanol	A	3681.4	3643.0	3627.9
II	Ethanol	$\left[\begin{smallmatrix} t \\ g \end{smallmatrix} \right]$ A	3676.1	(3636.0)	(3623.0)
		B	~3660.0	(3625.0)	(3611.5)
III	Propan-2-ol	$\left[\begin{smallmatrix} g \\ t \end{smallmatrix} \right]$ B	3660.0	(3626.0)	(3614.0)
		C	3637.4	(3610.0)	(3598.5)
IV	<i>t</i> -Butanol	C	3643.0	3616.0	3604.5
V	Pentan-3-ol, 2,2,4,4-tetramethyl	$\left[\begin{smallmatrix} g \\ t \end{smallmatrix} \right]$ D	3678.0	3650.5	3640.5
		F	3647.0	3623.5	3616.0
VI	Pentan-3-ol, 2,2,3,4,4-pentamethyl	$\left[\begin{smallmatrix} t \\ g \end{smallmatrix} \right]$ F	~3648	(3625.0)	(3618.0)
		E	3656.0	(3633.0)	(3622.5)
VII	Pentan-3-ol, 2,2,4,4-Me, 3- <i>t</i> -butyl	F	3651.0	3629.5	3622.5
VIII	Adamantan-1-ol	C	3631.0	3606.0	3593.9
IX	Cyclohexanol (<i>eq</i>)	$\left[\begin{smallmatrix} A_q \\ B_q \end{smallmatrix} \right]$ C	3636.0	(3615.0)	(3602.0)
		B	3652.5	(3623.5)	(3611.0)
X	Cyclohexanol (<i>ax</i>)	$\left[\begin{smallmatrix} A_x \\ B_x \end{smallmatrix} \right]$ —	—	—	—
		B	3654.0	3625.5	3614.0
XI	Cyclohexanol (<i>eq</i>), 2,6-dimethyl	$\left[\begin{smallmatrix} A_q \\ B_q \end{smallmatrix} \right]$ C	3626.0	3603.5	3591.0
		D	3668.0	3639.5	3628.5
XII	Cyclohexanol (<i>ax</i>), 2,6-dimethyl	$\left[\begin{smallmatrix} A_x \\ B_x \end{smallmatrix} \right]$ F	~3645	(3620.0)	(3612.0)
		D	3666.0	(3641.0)	(3629.0)
XIII	Cyclohexanol (<i>eq</i>), 1-methyl	$\left[\begin{smallmatrix} A_q \\ B_q \end{smallmatrix} \right]$ —	—	—	—
		C	3637.0	3610.5	3599.0
XIV	Cyclohexanol (<i>ax</i>), 1-methyl	$\left[\begin{smallmatrix} A_x \\ B_x \end{smallmatrix} \right]$ F	3646.0	(3620.0)	(3612.0)
		C	3639.5	(3613.0)	(3602.0)
XV	Cyclohexanol (<i>eq</i>), 2,2,6,6-tetramethyl	$\left[\begin{smallmatrix} A_q \\ B_q \end{smallmatrix} \right]$ F	~3646	(3625.0)	(3620.0)
		D	3666.5	(3641.5)	(3629.5)
XVI	Cyclohexanol (<i>eq</i>), 1,2,2,6,6-me	$\left[\begin{smallmatrix} A_q \\ B_q \end{smallmatrix} \right]$ F	3649.5	(3629.0)	(3625.0)
		E	3649.5	(3625.5)	(3615.0)

^aThe parentheses indicate that the frequency has been obtained by splitting of the overall OH band.

the present classification the gas—solvent shift can be regarded as specific for a particular OH environment. Furthermore as in general its magnitude decreases with increasing size of the α -substituent, vicinal to the OH proton, the shift can be related to the degree of accessibility of the OH group by solvent molecules. The specificity of the shift, however, is not directly connected with the concept of equivalent rotamers. As can be seen the OH rotamers within each of the classes B, C and F are equivalent but for the corresponding subclasses the shifts differ significantly and it is therefore justified to distinguish between them on this basis. For the rotamers of C1 and D, on the contrary, the shifts are essentially the same, notwithstanding their different OH proton environments. In view of this, another classification on the

Fig. 1. Projection in plane, perpendicular to the C—O bond of alcohol rotamers.

grounds of the magnitude of the shift may be more adequate than the present one, but we prefer to maintain the latter as given in Table 2, since it allows the corresponding shift for a given rotamer on the basis of its OH proton environment to be found easily.

In order to obtain gas-solvent shift values in a suitable form, we have established the shift averages for each (sub)class although the available data are not enough to be treated statistically. The averages prove to be reliable quantities, however, since ν_{diff} values derived from them lie within, or closely to the intervals established by Visser and van der Maas for similar rotamers [4].

As an illustration of the practical usefulness of the established shift averages we give two examples: the evaluation of the gas frequencies for the rotamers of 1,2-dimethylcyclohexanol in the *equatorial* conformation, and that of the solution values for the rotamers in *axial* 2-methyl cyclohexanol.

For the first compound a broad OH band is observed for the gas phase with maximum at 3639.5 cm^{-1} from which the different components cannot

TABLE 2

Characteristic intervals for ν_{OH} gas frequencies and gas-solvent shifts for saturated alcohols (cm^{-1})

Rotamer (sub)class	ν_{OH} frequency interval gas	ν_{OH} shift interval		ν_{OH} shift average		ν_{diff} (II - I)
		(g- CCl_4) (I)	(g- CS_2) (II)	(I)	(II)	
A (2)	3676-3681	38.4-40.1	53.1-53.5	39.0	53.5	14.5
B1 (2) ^a	3660	34.0-35.0	48.7-46.0	34.5	47.5	13.0
B2 (2) ^b	3652-3654	28.5-29.0	40.0-41.5	29.0	41.0	12.0
C1 (5) ^c	3631-3643	25.0-27.4	37.1-38.9	26.5	38.0	11.5 ^g
C2 (2) ^d	3626-3636	21.0-22.5	34.0-35.0	22.0	34.5	12.5 ^g
D (4)	3666-3678	25.0-28.5	37.0-39.5	26.5	38.0	11.5
E (2)	3649-3656	23.0-24.0	33.5-34.5	23.5	34.0	10.5 ^g
F1 (5) ^e	3646-3651	20.5-23.5	24.5-31.0	22.0	28.0	6.0 ^g
F2 (2) ^f	3645-3646	25.0-26.0	33.0-34.0	25.5	33.5	8.0 ^g

^aAcyclic alcohols only. ^bCyclohexanols in *equatorial* and *axial* conformation. ^cAll rotamers except A_q in cyclohexanols. ^d A_q rotamers only. ^eAll rotamers except A_x . ^f A_x rotamers only. ^gEstablished ν_{diff} intervals: for class C 11.5-12.5 cm^{-1} ; for class E 8.0-10.0 cm^{-1} ; for class F 4.5-8.0 cm^{-1} ; ref. 4.

be established [2]. In CCl_4 solution the band has been split into three subbands with frequencies at 3606.0, 3611.5 and 3618.0 cm^{-1} which are assigned to the rotamers A_q , C_q and B_q respectively [7]. If the solution values are incremented with the corresponding shifts, C2, C1 and E, gas frequencies of 3628.0, 3638.0 and 3641.5 cm^{-1} are obtained. These extrapolated values are consistent with the OH gas band observed, and can be regarded as reliable estimations for the frequencies of the different rotamers therefore.

For the second compound only one broad OH band is observed in CCl_4 solution, whereas for the gas phase two components are observed in the band with frequencies at 3660.5 and 3647.0 cm^{-1} corresponding respectively to the B_x and C_x , and to the A_x rotamers [2]. Applying the proper shifts for the classes D, B2 and F2, the frequencies in solution are estimated as 3633.5, 3631.5 and 3621.5 cm^{-1} . This is in excellent agreement with observation, since the OH band in CCl_4 has a maximum at 3632.0 cm^{-1} and a shoulder at about 3622 cm^{-1} [5].

CONCLUDING REMARKS

Our results show that the ν_{OH} gas-solvent shifts for the apolar solvents CCl_4 and CS_2 are characteristic for different kinds of OH rotamers in saturated alcohols. Therefore they can be employed for the accurate evaluation of the ν_{OH} frequency in solution for a given rotamer from the calculated gas value. Occasionally the reliability of calculated gas frequencies can be tested by comparison with gas values extrapolated from solution when the experimental

data for the former are not available. Although the accuracy of the established shift averages can be augmented by increasing the amount of available data, our values prove to give satisfactory results.

In addition since the ν_{OH} frequency and the gas—solvent shift appear to be independent, combination of these two parameters makes identification of the type of rotamer involved straightforward.

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