SOLVENT EFFECTS ON THE O-H STRETCHING BANDS OF ALCOHOLS

J. E. HOUSE, JR., and R. L. COOK
Department of Chemistry
Illinois State University, Normal

ABSTRACT. — The wavenumber of the O-H stretching vibration has been determined for nine aliphatic alcohols in the vapor phase and in heptane, carbon tetrachloride, carbon disulfide, and benzene. The extent of interaction between the alcohols and solvents has been related by means of the Kirkwood-Bauer equation. Results show that the much more basic benzene deviates markedly from the other solvents in its effect on the O-H band and, in fact, causes these bands to fall at the same wavenumber for all the alcohols studied. The effects of concentration on the monomer, dimer, and multimer bands of methyl alcohol are discussed.

It is well known that the O-H stretching band in the infrared spectra of alcohols occurs at lower wavenumbers in solvents than in the vapor phase. If there is a simple electrostatic interaction of an oscillating electric dipole with its surroundings of dielectric constant D, then the relative shift in going from the vapor phase to a solvent is proportional to $(D — 1)/(2D + 1)$ (Jones and Badger, 1951 and references therein). Usually this is written as (Josien and Fuson, 1954)

$$\frac{\overline{N}g - \overline{N}s}{\overline{N}g} = \frac{\triangle \overline{N}}{\overline{N}g} = C \frac{D-1}{2D+1} \quad (1)$$

where $\overline{N}s$ and $\overline{N}g$ are the stretching wavenumbers in the vapor phase

and in a solvent, respectively. Subsequently, it was suggested that the dielectric constant used should be that obtained at high frequency so that D is approximately the square of the index of refraction, n (Josien and Fuson, 1954). Equation (1) then becomes the usual form of the Kirkwood-Bauer equation

$$\frac{\triangle \overline{N}}{\overline{N}g} = C \frac{n^2-1}{2 n^2+1} \quad (2)$$

where C is the proportionality constant. In this study, the O-H stretching wavenumbers have been determined for a series of alcohols in the vapor phase and in several solvents to study solvent effects on the O-H stretching fundamental.

EXPERIMENTAL

The alcohols used in this work were either spectral or reagent grade. The solvents used were spectral grade carbon tetrachloride and carbon disulfide and reagent grade benzene and heptane. These chemicals were used without further purification. Solutions varied from about 0.02 to 0.04 molar depending on the alcohol except when studying concentration effects. The solution spectra were obtained using a cell with a path length of 0.41 mm. Vapor phase spectra were obtained in a gas cell of 10 cm path length using pressures of alcohol vapor varying from about 3 to 75 mm depending on the vapor pressure of the

alcohol at room temperature. All spectra were obtained at room temperature.

Infrared spectra were obtained in the range 3800-2800 cm^{-1} using a Beckman IR 8 grating spectrophotometer. The instrument used recorded linearly in wavenumber, and an auxiliary recorder was used for scale expansion. In order to provide absorption maxima for calibration, the spectrum in a given run was scanned from 3800 to 3200 cm^{-1} with the sample cell in the instrument. At 3200 cm^{-1} the cell was removed and a polystyrene film was placed in the instrument. The spectrum was then scanned to 2800 cm^{-1}, recording the polystyrene peaks on the same continuous spectrum which is linear in wavenumber. The polystyrene peaks at 3101, 3083, 3060, and 3003 cm^{-1} were used for calibration. The O-H stretching bands were usually quite sharp and easily positioned to within about ± 2 cm^{-1}. In benzene and in the vapor phase the bands were broader and could be positioned only to within about ± 4 cm^{-1}.

RESULTS

The positions of the O-H stretching bands of several alcohols are shown in Table 1. Some values for the positions of the O-H stretching

TABLE 1.—Wavenumbers of O-H Stretching Bands of Alcohols in Several Solvents and in the Vapor Phase.

Alcohol	Solvent[1]				
	Vapor	C_7H_{16}	CCl_4	CS_2	C_6H_6
Methyl	3687	3649	3642	3626	3607
Ethyl	3680	3642	3634[2]	3620	3603
n-Propyl	3677	3639	3636[2]	3621	3605
i-Propyl	3655	3631	3624	3612	3608
n-Butyl	3673	3641	3634	3619	3607
sec-Butyl	3658	3633	3627[3]	3613	3604
t-Butyl	3648	3620	3615	3603	3604
Cyclopentyl	3658	3630	3627	3611	3604
Cyclohexyl	3651	3626	3623	3610	3601

[1] Probable error about ± 2 cm^{-1} in all solvents except benzene. Error in vapor phase and benzene about ± 4 cm^{-1}.
[2] Motoyama and Jarboe (1966).
[3] Kuhn (1952).

bands were found in the literature for a few isolated cases, but no systematic determination has been made. For example, the positions of the O-H stretching bands of methyl, ethyl, and isopropyl alcohols in the vapor phase have been reported (Plyler, 1952; Falk and Whalley, 1961). Since the solvent usually used in hydrogen bonding studies is carbon tetrachloride, most of the O-H band positions have been reported in that solvent, and our results are in good agreement with previously reported values (Motoyama and Jarboe, 1966).

The infrared spectra of methyl alcohol at several concentrations are shown in Figure 1 for carbon tetrachloride solutions and in Figure 2 for carbon disulfide solutions.

DISCUSSION

At concentrations less than about 0.05 molar, the infrared spectrum of an alcohol in an inert solvent shows

only one peak, characteristic of the monomer alcohol. If the concentration is increased to 0.10 to 0.15 molar, peaks begin to appear at lower wavenumbers corresponding to alcohol molecules bonded in dimers. At still higher concentrations, peaks appear at still lower wavenumbers which correspond to O-H groups in higher aggregates (Van Ness, *et al.*, 1967). Figures 1 and 2 clearly show these characteristics for methanol in carbon tetrachloride and carbon disulfide.
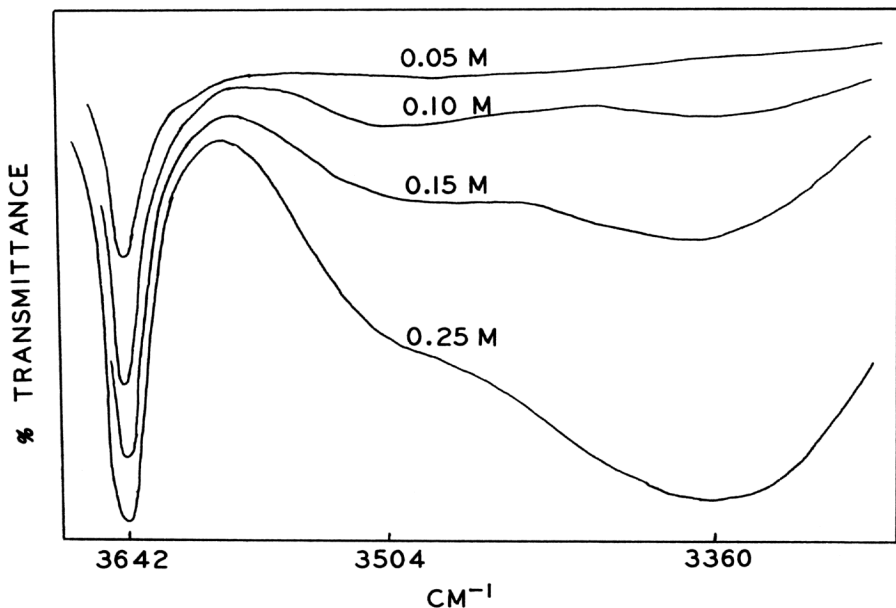

FIGURE 1. — Spectra of solutions of methyl alcohol in carbon tetrachloride.

Qualitatively, there are some interesting comparisons between the behavior of methyl alcohol in CCl_4 and CS_2. As can be seen from a careful study of the spectra in Figures 1 and 2, the curves in CS_2 are not only displaced toward lower wavenumbers but also are not exactly superimposable. In addition to the monomer O-H peak havings its maximum at a different wavenumber, the monomer peak is broader when the solvent is CS_2. This suggests that the O-H group is weakly hydrogen bonded to the solvent since hydrogen bonding leads to much broader O-H bands. It must also be bonded to CCl_4 but more weakly so. No variation in monomer peak position was observed with increasing concentration of alcohol in either solvent. A total of sixteen determinations of the position of the monomer O-H band showed a deviation from the mean of less than ± 2 cm^{-1}.

Another difference in the spectra is in the positions of the peaks corresponding to absorption by dimer and multimer O-H groups. This is more surprising than the difference between
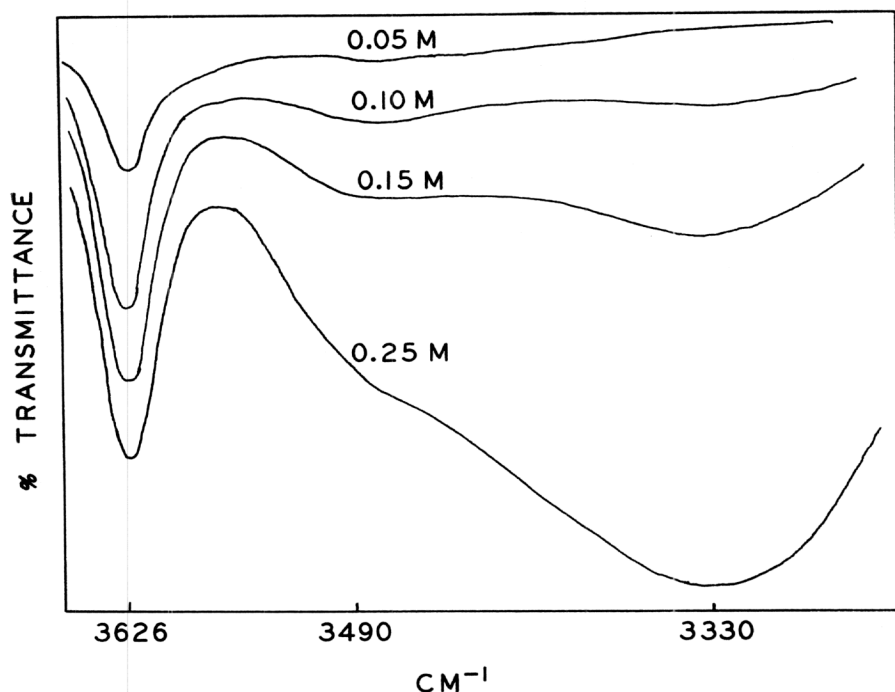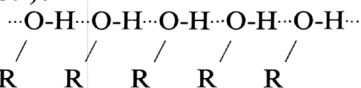
FIGURE 2. — Spectra of solutions of methyl alcohol in carbon disulfide.

the maxima of the O-H monomer peaks. In that case, the difference is due to the differences in electron donor properties of the solvent toward the unattached alcohol molecule. In the multimer unit, the alcohol molecules are linked (Henry, 1959).

···O-H···O-H···O-H···O-H···O-H···
   /   /   /   /   /
  R   R   R   R   R

Shifting the absorption maxima of the internal O-H groups to lower wavenumbers suggests that CS_2 solvates these multimer units more strongly than CCl_4. Otherwise one would expect that the monomer O-H absorption would be shifted to lower wavenumbers but not the multimer O-H band. In fact, the multimer O-H stretching band is shifted in CS_2 by about 30 cm^{-1} from its position in CCl_4.

When an alcohol molecule is hydrogen bonded to an electron donor molecule in solution, there is a large shift in the O-H stretching band to lower wavenumbers. In the gaseous state at low pressures the O-H bond is entirely free of all effects except those of the alkyl group. Between these two extremes there are weak interactions of the O-H group with a solvent, but these are usually not considered as actual hydrogen bonds unless the solvent has considerable ability to donate electrons. In these solvents the O-H stretching band is shifted by 30-80 cm^{-1} from where it might occur in the vapor state and by 10-50 cm^{-1} from where it might occur in an inert solvent.

The data in Table 1 show clearly that although carbon tetrachloride is the usual solvent used in hydrogen bonding studies (Pimentel and McClellan, 1960), it is not completely inert. The O-H band is shifted an average of about 5 cm^{-1} from its position in heptane. It is expected that a saturated hydrocarbon would be more nearly inert than carbon tetrachloride because of the unshared electron pairs on the chlorine atoms and the polarity of the C-Cl bonds. Carbon disulfide is less inert than carbon tetrachloride, shifting the O-H bands an average of about 19 cm^{-1} from their positions in heptane and about 14 cm^{-1} from their positions in CCl$_4$. These differences in the O-H band positions in the solvents used are presented in Table 2.

TABLE 2.—Differences in Alcohol O-H Band Wavenumber (cm^{-1}) With Solvent: A, Wavenumber in C$_7$H$_{16}$; B, Wavenumber in CCl$_4$; C, Wavenumber in CS$_2$; D, Wavenumber in C$_6$H$_6$.

Alcohol	O-H Band Position Difference, cm^{-1}					
	A-B[1]	A-C[1]	A-D[2]	B-C[1]	B-D[1]	C-D[2]
Methyl...............	8	23	42	15	34	19
Ethyl................	6	22	39	14	31	17
n-Propyl.............	3	18	34	15	31	16
i-Propyl.............	7	16	28	12	21	9
n-Butyl..............	7	22	33	15	26	11
sec-Butyl............	6	20	26	14	20	6
t-Butyl..............	5	17	16	12	11	—1
Cyclopentyl..........	3	19	26	16	23	7
Cyclohexyl...........	3	16	25	13	22	9

[1] Probable error about ±4 cm^{-1}.
[2] Probable error about ±6 cm^{-1}.

When the solvent is benzene, the O-H stretching band is shifted even farther toward lower wavenumbers, being 33-42 cm^{-1} lower for primary alcohols in benzene than in heptane, 25-28 cm^{-1} lower for the secondary alcohols, and 16 cm^{-1} lower for the one tertiary alcohol used. This indicates that the strength of the interaction of the O-H groups of alcohols with the solvent decreases as primary > secondary > tertiary. Further, it appears that for the primary alcohols used the strength of the interaction varies as methyl > ethyl > n-propyl > n-butyl when the solvents compared are heptane and benzene. This same order is found when the differences in peak positions in CS$_2$ and benzene are compared. It appears that primary alcohols have their O-H stretching bands shifted by 11-19 cm^{-1}, secondary alcohols by 6-9 cm^{-1}, and tertiary alcohols remain essentially unchanged. Again the shifts indicate that for primary alcohols, the order of decreasing solvent effect is methyl > ethyl > n-propyl > n-butyl. However, the magnitudes of the errors are such that the differences between the primary alcohols fall within the limits of error and this order is not followed for all solvent pairs. Although this trend is followed

for the two solvent pairs, the primary alcohols are all affected to the same extent. Considering the behavior in the other solvent pairs shows that either most of the shifts are about the same or that the errors are large enough to prohibit observing a trend similar to that just described. It does appear that there is a trend showing the solvent effects on the O-H band of alcohols in the order primary > secondary > tertiary and this trend is too large to be experimental error where the difference in solvent is large; e.g., the difference between heptane and benzene or carbon tetrachloride and benzene, shown as columns A-D and B-D in Table 2.

The influence of solvent on the O-H stretching band is further illustrated by a plot of equation (2) for the several solvents (Jones and Badger, 1951). For the four solvents used, the values of the function $(n^2 - 1)/(2n^2 + 1)$ are 0.190, 0.216, 0.228, and 0.263 for heptane, CCl_4, C_6H_6, and CS_2 respectively. Figure 3 shows this plot for the solvents used. The points represented are for methyl alcohol, but the points for all the primary alcohols are almost exactly superimposable. A similar plot for the secondary alcohols gives a line displaced somewhat to the left because of the smaller O-H band shifts for these alcohols. The points for the secondary alcohols are not as nearly superimposable as for the primary alcohols.

It is interesting that in all cases the point for benzene falls far off the line, indicating that the shift of the O-H band is larger than expected for that solvent. Aromatic molecules have considerable basicity (Tamres, 1952)
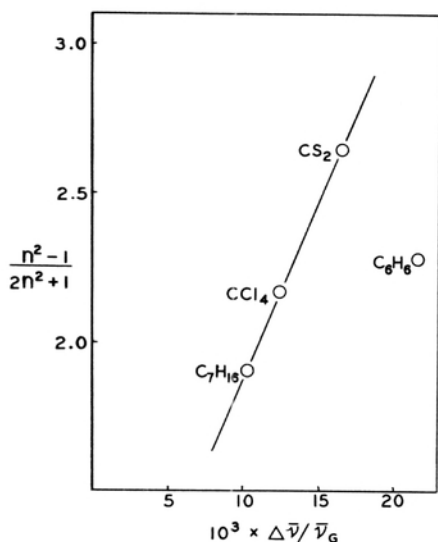

FIGURE 3. — A plot of $(n^2 - 1)/(2n^2 + 1)$ *vs* $\Delta \bar{N}/\bar{N}_g$ for methyl alcohol in several solvents.

and this is reflected by the larger O-H shift.

One further point should be mentioned. In the vapor, heptane, CCl_4, and CS_2, methyl alcohol has the O-H stretching band at 3687, 3649, 3642, and 3626 cm^{-1} respectively, while those for t-butyl alcohol are 3648, 3620, 3615, and 3603 cm^{-1}. All the other O-H bands falls between these two extremes. In benzene solutions, all the O-H bands fall at the same position, 3604 ±4 cm^{-1}. Thus, it appears that benzene removes the effect of the alkyl group on the O-H stretching band. Assuming that the O-H groups interact equally with benzene molecules, this means that solvation of the alkyl groups must create the same electronic environment of the O-H group in all the alcohols. This behavior is currently under investigation using nuclear resonance techniques.

ACKNOWLEDGMENTS

LITERATURE CITED

FALK, M., and E. J. WHALLEY. 1961. Infrared Spectra of Methanol and Deuterated Methanols in Gas, Liquid, and Solid Phases. J. Chem. Phys., *34*, 1554-1568.

HENRY, L. 1959. Relation Entre Les Modifications Par Liaison Hydrogene Des Frequences De Valence Des Hydroxyles Et Leur Constante De Dissociation. Hydrogen Bonding. D. Hadzi, Editor. Pergamon Press, N. Y. p. 163.

JONES, L. H., and R. M. BADGER. 1951. The Frequency of the Third Harmonic O-H Band of Methanol in Various Solvents and the Hydrogen Bonding of Methanol With Aromatic Hydrocarbons. J. Am. Chem. Soc., *73*, 3132-3134.

JOSIEN, M. L., and N. FUSON. 1954. Infrared Study of the Effect of Solvent Upon $\overline{N}$ (NH) in Pyrrole. J. Chem. Phys., *22*, 1169-1177.

————. 1954. A New Analysis of the Effect of Polar Solvents Upon $\overline{N}$ (NH) in Pyrrole. J. Chem. Phys., *22*, 1264-1265.

KUHN, L. P. 1952. The Hydrogen Bond. I. Intra- and Intermolecular Hydrogen Bonds in Alcohols. J. Am. Chem. Soc., *74*, 2492-2499.

MOTOYAMA, I., and C. H. JARBOE. 1966. Hydroxyl Group Stretching Frequency and Extinction Coefficient Studies on Aliphatic Alcohols. J. Phys. Chem., *70*, 3226-3228.

PIMENTEL, G. C., and A. L. McCLELLAN. 1960. The Hydrogen Bond. W. H. Freeman and Co., San Francisco xii + 475 pp.

PLYLER, E. K. 1952. Infrared Spectra of Methanol, Ethanol, and n-Propanol. J. Res. Nat. Bur. Stand., *48*, 281-286.

TAMRES, M. 1952. Aromatic Compounds As Donor Molecules in Hydrogen Bonding. J. Am. Chem. Soc., *74*, 3375-3378.

Manuscript received August 17, 1968.