and Walden[14] reports $[\alpha]^{18}\text{D}$ −167° (chloroform) for this substance. The methyl L-(+)-mandelate, b.p. 95–97° (1 mm.), $[\alpha]^{25}\text{D}$ 171.4° (*c* 1.833, chloroform), was obtained in 87% yield. One gram of this recrystallized from petroleum ether (20 ml.) gave 0.91 g. of the pure ester, m.p. 55.5°, $[\alpha]^{25}\text{D}$ 173.5° (*c* 0.968, chloroform).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.00; H, 6.09. Found: C, 64.91; H, 5.98.

Methyl O-Methyl-L-(+)- and O-Methyl-D-(−)-mandelates (XVI and XXIII).—Unrecrystallized methyl D-(−)-mandelate (9.05 g.), methyl iodide (40 ml.), silver oxide (15 g.), Drierite (10 g.) and glass beads (10 g.) were stirred under reflux with calcium chloride tube protection for 24 hours. After diluting with chloroform, filtering, rinsing the cake with chloroform, and distilling the solvents *in vacuo* there remained 9.59 g. (98%) of crude product, $[\alpha]^{24}\text{D}$ −89.1° (*c* 1.111, acetone). McKenzie and Wren[15] give $[\alpha]^{13}\text{D}$ −96.3° (acetone) for pure methyl O-methyl-D-(−)-mandelate. Methyl L-(+)-mandelate was methylated by the same procedure with identical results. The crude product was distilled, b.p. 79–88° (1 mm.), and a middle cut taken for rotation and analysis; $[\alpha]^{23}\text{D}$ was 88.7° (*c* 1.070, acetone).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 66.70; H, 6.74. Found: C, 66.59; H, 6.76.

O-Methyl-L-(+)- and O-Methyl-D-(−)-mandelic Acids (XIII and XX).—Since alkaline hydrolysis of the above methyl esters may be attended by a certain amount of racemization,[16] these were hydrolyzed under acidic conditions, where the extent of racemization was found not very marked. Methyl O-methyl-D-(−)-mandelate (4.00 g.) was refluxed for three hours with water (30 ml.) containing sulfuric acid (1.25 ml.). The mixture was cooled, saturated with salt, and extracted twice with chloroform. The extract was dried over anhydrous sodium sulfate, filtered, and the solvent distilled *in vacuo* to yield 3.28 g. (89%) of crude, amber oil, $[\alpha]^{22}\text{D}$ −144.0° (*c* 1.174, ethanol), which crystallized spontaneously. This was dissolved in 55–85° petroleum ether (100 ml.), the solution decanted from a small amount of sludge and slowly cooled. The product crystallized as splendid long needles. Another recrystallization gave 2.10 g. of practically pure product, m.p. 65–66°, $[\alpha]^{25}\text{D}$ −148.4° (*c* 1.025 ethanol). McKenzie and Wren[14] give m.p. 63–64°, $[\alpha]^{17}\text{D}$ −150.1° (ethanol) for O-methyl-D-(−)-mandelic acid. Hydrolysis of methyl O-methyl-L-(+)-mandelate by the same procedure gave similar results. After two recrystallizations from petroleum ether the product had m.p. 64–65° and $[\alpha]^{25}\text{D}$ 149.4° (*c* 0.964, ethanol).

Infrared Absorption Spectra.—The infrared absorption spectra of the O-methyl-L-(+)-mandelic acid prepared synthetically above and of the sample prepared before by degradative means were determined with a Perkin–Elmer Infrared Spectrometer in the region 8–15 μ. The samples were prepared by grinding into a mineral oil suspension as recommended by Kuhn.[17] The author is indebted to his colleague, Dr. John H. Wise, for determination of these spectra.

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(14) P. Walden, *Ber.*, **38**, 400 (1905).

(15) A. McKenzie and H. Wren, *J. Chem. Soc.*, **97**, 484 (1910).

(16) A. McKenzie and H. Wren, *ibid.*, **115**, 611 (1919).

(17) L. P. Kuhn, *Anal. Chem.*, **22**, 276 (1950).

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The Frequency of the Third Harmonic O–H Band of Methanol in Various Solvents, and the Hydrogen Bonding of Methanol with Aromatic Hydrocarbons

BY LLEWELLYN H. JONES AND RICHARD M. BADGER

The absorption spectra of dilute solutions of methanol in several solvents have been observed in the region of the third harmonic of the OH band. In non-polar solvents the OH frequency is shifted from its position in the vapor by an amount proportional to $(D - 1)/(2D + 1)$ where D is the static dielectric constant of the medium. In certain polar chlorinated solvents the frequency shift is less, but in aromatic solvents the large shift is taken as an indication of hydrogen bond formation.

Introduction

Though benzene has sometimes been regarded as an inert solvent, and has indeed been used as a medium in which to investigate the association of substances by hydrogen bonding,[1] it was some time ago pointed out that this liquid appears to exhibit an interaction with proton donor substances which may probably be described as the formation of a weak hydrogen bond.[2] Evidence for this interaction is the fact that phenol, for example, is much less strongly associated in benzene than in carbon tetrachloride. Furthermore, the fundamental and harmonics of the OH valence vibration of the unassociated alcohol molecules are found at considerably lower frequencies in the former solvent than in the latter.[3,4,5]

In dilute solutions of an alcohol in an organic solvent one finds that the frequency of the OH band is in general somewhat less than in the vapor state. If there is a simple electrostatic interaction of the oscillating dipole with its surroundings of dielectric constant D, the frequency shift will be comparatively small and Kirkwood[6] has shown that it should be approximately proportional to $(D - 1)/(2D + 1)$.[7] Where the shift is much larger, an interaction of a different character appears to be indicated.

It has seemed of interest to investigate further the interaction between proton donor substances and aromatic hydrocarbons and in particular to study the effect of substitution. Consequently the third harmonic of the OH band of methanol has been observed in solutions of this alcohol in benzene, toluene, *m*-xylene, mesitylene, pseudocumene and α-methylnaphthalene. For comparison purposes several non-aromatic solvents also were employed. As will be seen later, these fall into two classes; one of these includes the non-polar substances, carbon tetrachloride, *n*-hexane and cyclohexane, and the other the halogenated hydrocarbons,

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(1) E. N. Lassetre and R. G. Dickinson, THIS JOURNAL, **61**, 54 (1939).

(2) R. M. Badger, *J. Chem. Phys.*, **8**, 288 (1940).

(3) A. Naherniac, *Ann. phys.*, **7**, 528 (1937).

(4) Kreuzer and Mecke, *Z. physik. Chem.*, **B49**, 309 (1942).

(5) See also W. Lüttke and R. Mecke, *Z. Elektrochem.*, **53**, 241 (1949).

(6) J. G. Kirkwood, private communication.

(7) The dielectric constant to be used here is the static value. In discussing shifts of frequency where an electronic transition is involved this will not be appropriate. Cases of this sort have recently been discussed by N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

chloroform, pentachloroethane and *sym*-tetrachloroethane.

Experimental

The spectra were photographed on Eastman 1Z infrared plates sensitized with 3% ammonia solution, using a Bausch and Lomb Littrow spectrograph with glass prism giving a dispersion of 64 cm.$^{-1}$ per mm. in the region of interest. A 500-watt tungsten projection lamp was used as source with exposure times from 2 to 3 minutes. An arc comparison spectrum containing infrared lines of sodium, potassium, calcium, barium, strontium and chromium was photographed alongside each absorption spectrum.

Since aromatic hydrocarbons have weak absorption bands near the third harmonic of the OH band of methanol it was found desirable to employ the following procedure to reduce interference. For each aromatic solvent a sequence of three exposures was taken, using two absorption cells in series, as follows: (1) 19 cm. of 1 volume formal methanol in carbon tetrachloride and 19 cm. of the aromatic hydrocarbon; (2) 19 cm. of carbon tetrachloride and 19 cm. of 1 vf. methanol in the aromatic hydrocarbon; (3) 19 cm. of carbon tetrachloride and 19 cm. of the aromatic hydrocarbon.

Figure 1 presents microphotometer tracings of these spectra in which the solid lines indicate the first two exposures of a sequence, and the dotted line the solvent background in the neighborhood of the OH band.

In Table I are given the wave lengths of the absorption maxima of the third harmonic OH band in each of the several solvents, together with the dielectric constant of the solvent.

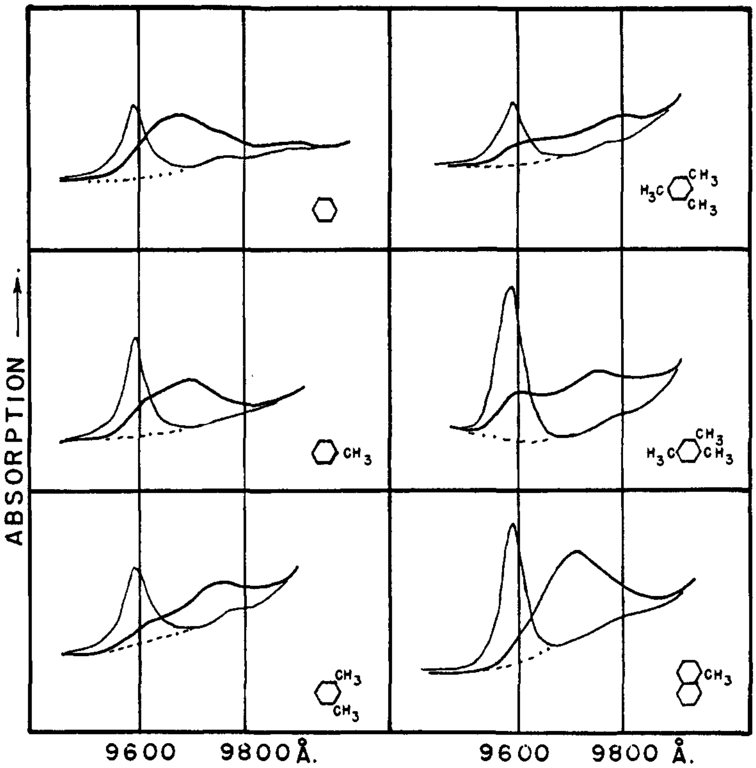

Fig. 1.—Absorption in the region of the third harmonic of the O–H band in the indicated solvents compared with the single narrow peak in CCl_4 solutions. The dashed line represents solvent background.

TABLE I

THE SHIFT IN THE THIRD HARMONIC O–H BAND OF METHANOL IN VARIOUS SOLVENTS

Solvent	$\nu_{max.}$ (cm.$^{-1}$)	$\nu_{vap.} - \nu_{soln.}$	D_{25}[a]	$\Delta\nu[(2D+1)/(D-1)] \times 10^{-2}$
CCl_4	10,428	109	2.229	4.9
n-Hexane	10,449	88	1.865	4.8
Cyclohexane	10,438	99	2.039	4.8
$CHCl_3$	10,392	145	4.85	4.0
C_2HCl_5	10,403	134	3.55	4.3
sym-$C_2H_2Cl_4$	10,381	156	7.61	3.8
Benzene	10,324	213	2.268	9.3
Toluene	10,311	226	2.369	9.5
		(150)		(6.3)
α-Methylnaphthalene	10,295	242	(2.6)[b]	(9.4)
Mesitylene	10,200	337	2.337	14.3
	10,403	134		5.7
Pseudocumene	10,237	300	2.414	12.4
	10,427	110		4.6
m-Xylene	10,245	292	2.359	12.3
	10,411	126		5.3
Methanol vapor	10,537	0		

[a] From "Int. Crit. Tables." [b] Estimated.

Discussion

In Fig. 2 is plotted the difference in frequency of the third harmonic OH band of methanol in the vapor state and in solution *versus* $(D - 1)/(2D + 1)$, where D is the dielectric constant of the solvent. The points for carbon tetrachloride, hexane and cyclohexane lie on a straight line extrapolating to the origin, as should be expected from the Kirkwood relation. The slope of this line should in principle be predictable, but the necessary information regarding the potential function and dependence of dipole moment on nuclear distances is not now available for the methanol molecule. Consequently, the three points above mentioned will be regarded as determining empirically the relation between frequency shift and dielectric constant in non-polar liquids.

In the aromatic solvents a frequency shift occurs which is in each case very considerably greater than predicted by this relation, and is indeed of the order of magnitude observed when a hydrogen bond is formed between two oxygen atoms. We regard this as evidence that methanol molecules are bonded to aromatic hydrocarbon molecules by a hydrogen bond of moderate strength involving the hydroxyl hydrogen.

In the more highly substituted hydrocarbons, mesitylene, pseudocumene and *m*-xylene, the OH harmonic band is clearly a doublet, with components of nearly equal intensity. The toluene spectrum indicates the presence of a high frequency component which is incompletely resolved and has a somewhat lower intensity than its companion. This may also possibly be the case in α-methylnaphthalene, though the intensity is in any case much less. In Fig. 2 the more highly shifted maxima are represented by open circles and the high frequency components by small black circles. It will be seen that the latter fall within experimental error on the curve representing behavior in non-polar solvents.

We attribute the two maxima to the presence of two kinds of solute molecules, some of which have

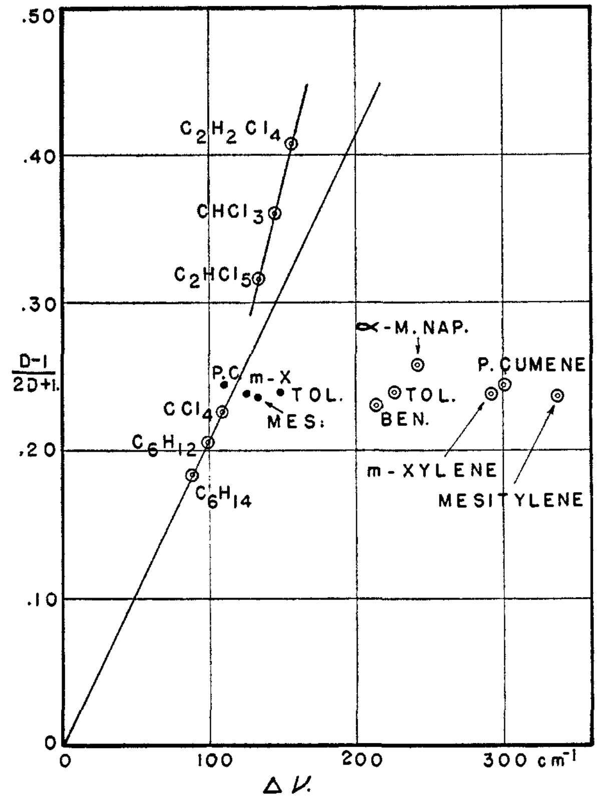

Fig. 2.—Frequency shift from vapor to solution of the third harmonic O–H band of methanol *versus* $(D - 1)/(2D + 1)$ of the solvent. The small solid circles indicate the high frequency component where a doublet structure is observed.

interacted strongly with the solvent and some of which have not. It appears that the substitution of methyl groups in the aromatic solvents both increases the strength of the hydrogen bond which can be formed with methanol, but by steric effects decreases the probability that it will be formed.

This interpretation is supported by some observations on the effect of temperature on the OH harmonic bonds. Since it was not practical to study solutions of methanol over any considerable temperature range a 0.4 volume formal solution of cyclohexanol in pseudocumene was observed at three rather widely spaced temperatures with the results shown in Fig. 3. Here again a doublet band appears of which the high frequency component increases greatly in intensity with temperature at the expense of its companion.

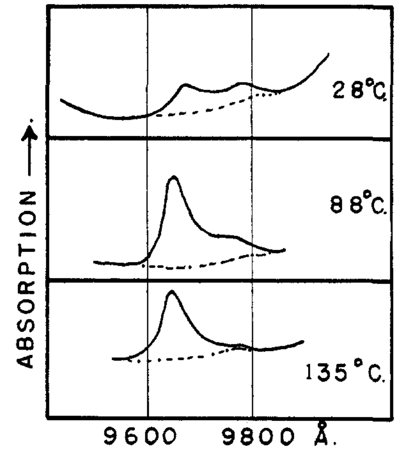

Fig. 3.—Absorption spectrum of a 0.4 volume formal solution of cyclohexanol in pseudocumene at three temperatures.

The chlorinated polar solvents, chloroform, *sym*-tetrachloroethane and pentachloroethane fall in a third and interesting group, as they produce frequency shifts less than would be expected in non-polar solvents. The simple Kirkwood relation is presumably not applicable in these cases but it may be further noted that the hydrogen of chloroform most certainly forms a hydrogen bond with the oxygen of methanol, which may be expected to affect appreciably the hydroxyl frequency. A similar situation possibly occurs in the other chlorinated solvents.

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