

Influence of solvents on the -OH and >C=O stretching frequencies of benzoin and methyl mandelate

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ABSTRACT

The influence of solvents on the intramolecular hydrogen bond in benzoin and methyl mandelate is studied using infrared spectroscopy. Non-oxygenated solvents could not break the chelation but could shift the OH frequencies to a small extent. Oxygenated solvents like diethyl ether, acetone and dioxan could break the chelation and form intermolecular hydrogen bonds. The relative intensities of the bands of intra and intermolecular hydrogen bonds gave an indication of the donor ability of these solvents, which is linked with their capacity to break the intramolecular hydrogen bonding. Making use of the symmetry numbers of the OH band, the order of the interacting abilities of the oxygenated solvents in breaking the chelation is ascertained and explained.

1. INTRODUCTION

IN the *pmr* studies on the influence of solvents on the OH proton chemical shifts of benzoin and methyl mandelate, Rao *et al.*¹ observed that in strong proton accepting solvents like dimethylformamide and dimethyl sulfoxide, chelation in these compounds breaks and an intermolecular hydrogen bond is formed between OH of these compounds and the solvent molecules. As the *pmr* measurements failed to indicate the inter and intramolecular hydrogen bonded species separately the problem is further investigated by *ir* spectra and the results are incorporated in this paper. Solvents of a wide range of polarities and proton accepting abilities are included to find which solvents are capable of breaking chelation.

2. EXPERIMENTAL

The *ir* spectra are recorded on Perkin-Elmer 337 grating spectrophotometer (wave number linear) at slow speed using 0.5 mm sodium chloride matched cells. The concentrations of the solutions used are of the order of 0.1 molar and the ambient temperature is $38^\circ \pm 2^\circ$ C. Cyclohexane,

carbon tetrachloride, methylene chloride, are of spectrograde. Anisole, acetophenone, diphenyl ether are either Merck or BDH quality and are distilled before use and the middle fractions are collected. Chloroform, diethyl ether, dioxan, acetone and acetonitrile are purified by the methods available in the literature². Benzophenone, being a solid, its saturated solution in carbon tetrachloride is used as a solvent. In the study of ternary mixtures, the mixture of the solvents of the same composition is placed in the reference beam, to compensate for the solvent absorption. For benzoin and methyl mandelate the -OH and >C=O frequencies (ν), half band widths ($\Delta\nu_{1/2}$) and band symmetry numbers (α/β) are given in tables 1 and 2 respectively. Band symmetry is expressed as the ratio of segments of the half band widths on the high (α) and low (β) frequency sides of the band maximum. The half band widths are measured at $0.5 \epsilon_{\text{max}}$. The measurements are accurate up to $\pm 2 \text{ cm}^{-1}$.

3. DISCUSSION

Benzoin contains -OH and >C=O groups which are involved in intramolecular hydrogen bond leading to the formation of a five atom chelate^{1,3}. In carbon tetrachloride solution, benzoin exhibits single, sharp, and symmetrical vibrational bands for OH and >C=O groups at 3462 cm^{-1} and 1681 cm^{-1} respectively. These therefore correspond to intramolecularly bonded groups³.

In all the other solvents the >C=O band continues to be sharp and symmetrical as indicated by its half band width and symmetry numbers (table 1). It is not quite sensitive to the solvent polarity. The OH band on the other hand is affected markedly by the solvents. As in carbon tetrachloride, in other non-oxygenated solvents, *viz.*, cyclohexane, chloroform, methylene chloride and acetonitrile, it is symmetrical and sharp. It appears as a doublet in diethyl ether and acetone (figure 1). In each of

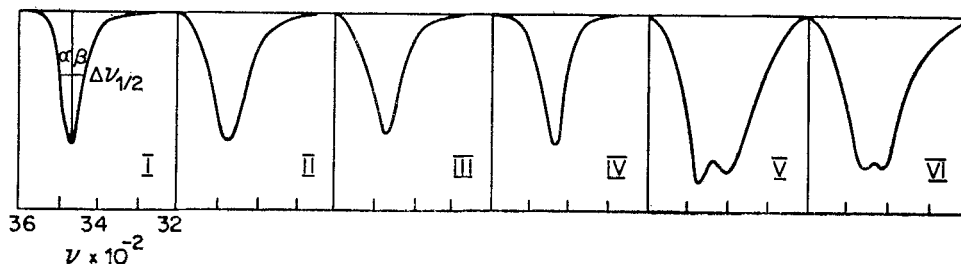


Figure 1. The OH stretching vibration bands of benzoin in different solvents: I. Carbon tetrachloride; II. Chloroform; III. Anisole; IV. Acetonitrile V. Diethyl ether; VI. Acetone,

Table 1. Infrared data of benzoin

Sl. No.	Solvent	ν_{OH} cm ⁻¹	$\Delta \nu_{\frac{1}{2}}$ cm ⁻¹	symmetry number α/β	$\nu_{>\text{C}=\text{O}}$ cm ⁻¹	$\Delta \nu_{\frac{1}{2}}$ cm ⁻¹	symmetry number α/β
1.	Cyclohexane	3472	40	1	1684	10	1
2.	Carbon tetra- chloride	3462	67	1	1681	10	1
3.	Chloroform	3458	100	1	1680	11	1
4.	Methylene Chloride	3453	90	1	1680	11	1
5.	Acetonitrile	3451	110	1	1682	11	1
6.	Anisole	3460	75	0.87	1680	11	1
7.	Diphenyl ether	3460	75	0.95	1680	12	1
8.	Diethyl ether	3460 3404 (S)*	165	..	1680	15	1
9.	Dioxan	3404	145	1.3	1680	16	1
10.	Acetone	3455 3402 (S)*	145
11.	Acetophenone	3458	117	0.6
12.	Benzophenone	3460	78	0.91

*S = Shoulder.

the solvents, *viz.*, anisole, diphenyl ether, dioxan, acetophenone and benzophenone only one OH band is observed. It is unsymmetrical as indicated by the symmetry number.

The observed changes in the OH band of benzoin may be explained in terms of interaction between solvent molecules and the OH of the chelate. When the chelate is placed in a solvent, the molecules of the latter begin to interact with the OH of the former. Thus the hydrogen of the OH group is under a competitive pull of the solvent molecules on the one hand and existing pull of the carbonyl oxygen on the other. However, when the pull of the solvent molecules becomes stronger than the strength of intramolecular hydrogen bond, the latter cleaves and the intermolecular hydrogen bond is formed between OH and the solvent as shown in species

III (Chart I). If the pull of the solvent is weaker than the strength of intramolecular hydrogen bond of the chelate the latter exists as species I. In cases where the solvent interaction is not so strong as to break the intramolecular hydrogen bond, but could tagg on to the OH of the benzoin by electrostatic attraction, species II of chart I may arise. In this situation, hydrogen of OH experiences simultaneous pull of the carbonyl oxygen and the solvent molecule. In a particular solvent depending upon its interacting ability there may exist species I alone, or species III alone, or I along with III or I along with II in varied proportions. As each of the species gives rise to characteristic OH bands, it would be possible to identify the type of species present in any solvent.

In diethyl ether and acetone, benzoin exhibits two OH bands one around 3458 cm^{-1} and the other around 3404 cm^{-1} . The high frequency bands in these solvents are closer to the one observed in carbon tetrachloride solution and should therefore correspond to intramolecularly bonded OH as in species I. The low frequency bands are closer to the frequency of OH of diphenyl carbinol in these solvents⁴. They may therefore correspond to intermolecularly bonded OH as in species III. This was confirmed by the study of spectra in mixed solvents (carbon tetrachloride: diethyl ether/acetone). In mixtures containing low proportion of ether, the low frequency band is observed as a mere shoulder. With increase in propor-

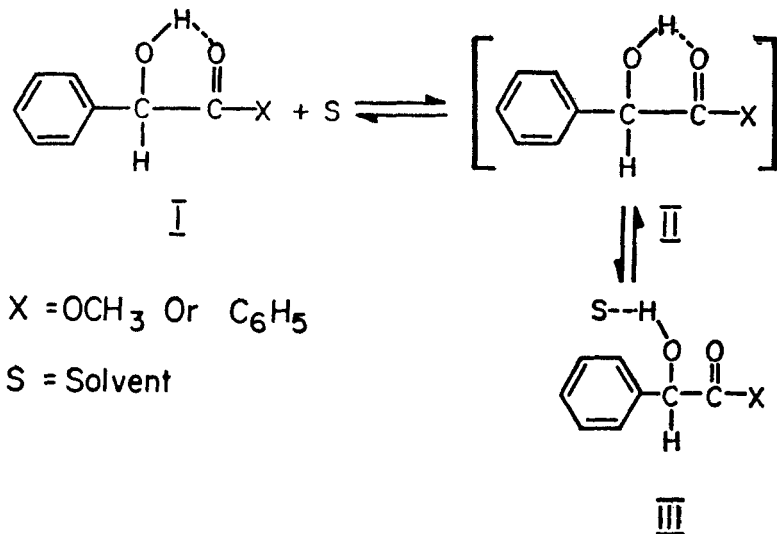


Chart I. Interaction of solvent with the intramolecular hydrogen bonded OH of benzoin and methyl mandelate.

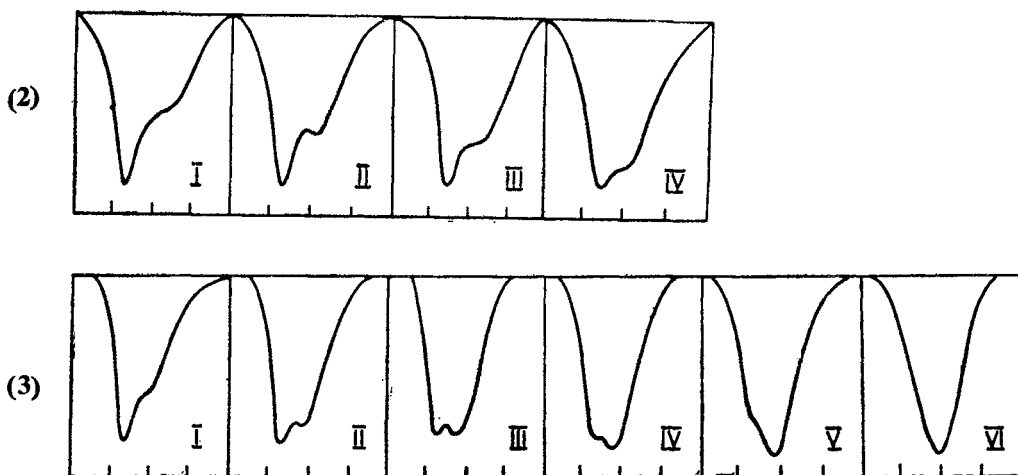


Figure 2. The OH stretching vibration bands of benzoin in solutions of different proportions of carbon tetrachloride and diethyl ether: I. 0.3 ml of diethyl ether in 1 ml of CCl_4 ; II. 0.5 ml of diethyl ether in 1 ml of CCl_4 ; III. 0.7 ml of diethyl ether in 1 ml of CCl_4 ; IV. 0.9 ml of diethyl ether in 1 ml of CCl_4 .

Figure 3. The OH stretching vibration bands of benzoin in solutions of different proportions of carbon tetrachloride and dioxan: I. 0.1 ml of dioxan in 1 ml of CCl_4 ; II. 0.2 ml of dioxan in 1 ml of CCl_4 ; III. 0.3 ml of dioxan in 1 ml of CCl_4 ; IV. 1.0 ml of dioxan in 1 ml of CCl_4 ; V. Complete dioxan.

tion of diethyl ether the intensity of low frequency band increased (figure 2). The changes are quite analogous with acetone and carbon tetrachloride mixtures. From this it is clear that acetone and ether solutions contain both species I and III. As the intensities of the two bands are almost the same, it may be inferred that the two species are present approximately in equal proportion.

Usually the >C=O frequency is expected to increase on the rupture of intramolecular hydrogen bond; strangely this is not observed. It may be due to a small difference in the frequency of >C=O bands of chelated and unchelated systems, *viz.*, >C=O frequencies of benzoin and deoxybenzoin are 1681 and 1685 cm^{-1} respectively. The expected small increase of 4 cm^{-1} in >C=O frequency on the rupture of chelation is probably offset by the lowering caused by the polar solvent. The >C=O frequencies are generally lower in polar solvents than in non-polar solvents⁵.

In dioxan, benzoin is found to exhibit only one OH band, the frequency of which is the same as the low frequency band observed in diethyl ether. This band as in diethyl ether solution may be assigned to OH band

Table 2. Infrared data of methyl mandelate

Sl. No.	Solvent	ν_{OH} cm^{-1}	$\Delta \nu_{\frac{1}{2}}$ cm^{-1}	symmetry number α/β	$\nu_{>\text{C=O}}$ cm^{-1}	$\Delta \nu_{\frac{1}{2}}$ cm^{-1}	symmetry number α/β
1.	Cyclohexane	3540	27	1	1740	11	1
2.	Carbon tetra- chloride	3540	45	1	1740	20	1
3.	Chloroform	3538	65	1	1740	22	1
4.	Methylene chloride	3530	66	1	1740	22	1
5.	Acetonitrile	3480	130	1.15	1745	30	1
6.	Anisole	3521	115	0.67	1738	22	1
7.	Diphenylether	3520	66	1.0	1740	25	1
8.	Diethylether	3535 (S)* 340	143	..	1745	30	1
9.	Dioxan	3405	145	1.2	1745	25	1
10.	Acetone	3470 3405	180
11.	Acetophenone	3470 3405	190	0.55
12.	Benzophenone	3527	99	0.64

*S = Shoulder

of the species III. The band is broad ($\Delta \nu_{\frac{1}{2}} = 145 \text{ cm}^{-1}$) and unsymmetrical ($\alpha/\beta = 1.3$). The asymmetry of the band may usually be due to overlap of two or more component bands each of which may be symmetrical⁶. From the symmetry number which is greater than 1 it might be inferred that a low intense band might be hidden under the high frequency wing of the main band. This prediction is found to be true when the spectra are recorded in mixed solvents. In a 1:1 (v/v) mixture of carbon tetrachloride and dioxan two bands are observed (figure 3). The high frequency band observed is similar to the one observed in carbon tetrachloride solution and the low frequency band appeared at 3404 cm^{-1} as in the case of diethyl ether. The relative intensities of the two bands are found to depend on the composition of the solvent mixture. With the increase in proportion of

dioxan, the intensity of high frequency band is found to decrease and that of the low frequency band increase. These findings clearly establish the presence of a high frequency band lying under the main band. Unlike in diethyl ether solution, the low frequency band in dioxan is far more intense than the high frequency band. This shows that dioxan solution contains relatively larger proportion of species III as compared to diethyl ether solution.

As in the case of dioxan, single OH band is observed in anisole, diphenyl ether, acetophenone and benzophenone. The frequencies of the observed bands are closer to the one in carbon tetrachloride and therefore correspond to species I. However, the bands are not symmetrical as indicated by their symmetry numbers. From the symmetry numbers which are less than 1 it may be presumed that some low intense bands might lie under the low frequency wing of the main band. These low frequency bands may arise due to the presence of species II, together with a small proportion of species III. The partial overlap of these low frequency bands with the main band might result in the asymmetry of the band.

The interaction of non-oxygenated solvents is too weak to break the chelation but it could bring about small shifts in OH frequency. When chelation is intact, the shifts in ν_{OH} in different solvents should correspond to the dielectric constant of the solvent⁴. If this is true a linear relation should be obtained between $\Delta\nu_{\text{OH}}$ and the dielectric constant of the solvent. In fact the plot of $\Delta\nu_{\text{OH}}$ ($\nu_{\text{OH cyclohexane}} - \nu_{\text{OH solvent}}$) vs dielectric constant of these solvents gave a straight line, (figure 4) the slope of which, however is very small indicating that the dielectric constant plays a very small role in altering the frequency of intramolecularly bonded OH.

Of the doublets in acetone and ether solutions, the high frequency bands which correspond to species I obey the linear relation, whereas the low frequency bands do not. This may be explained on the basis of solvent shifts of OH in species III on account of local association as well as dielectric constant.

From the above observations it is clear that the interacting abilities of different solvents with the chelate vary. The interaction of non-oxygenated solvents with the chelate is quite small and the chelate remained stable in these solvents. The interaction of diethyl ether, acetone and dioxan is strong enough to break chelation and form species III, the proportion of which corresponds to the strength of interaction. Examination of the relative intensities of the bands due to species I and III in these solvents reveal that the interacting abilities of these solvents fall in the order

Dioxan > acetone > diethyl ether

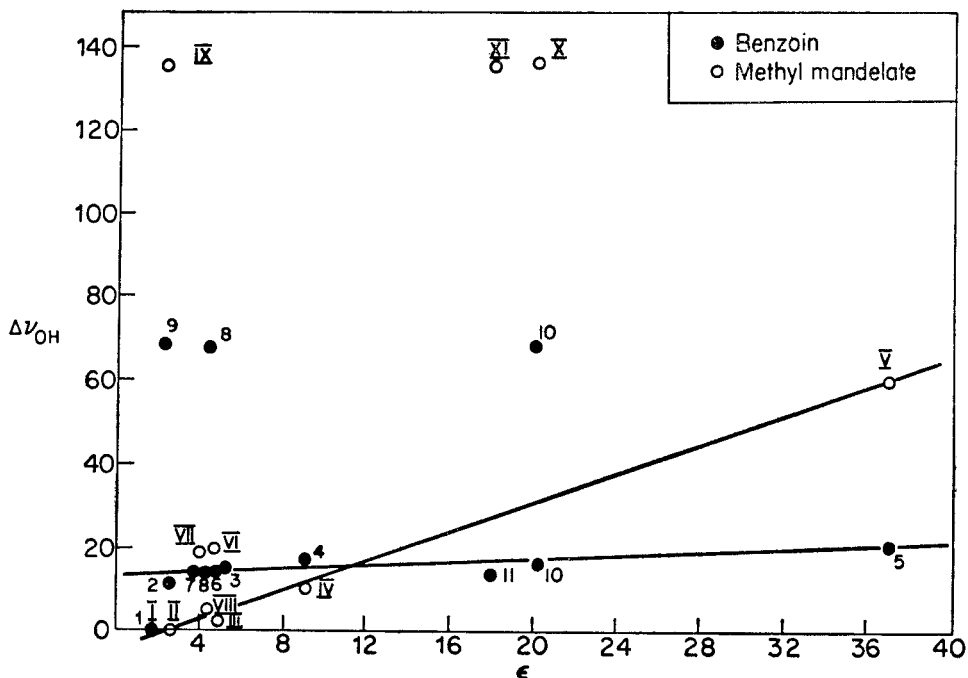


Figure 4. Plot of $\Delta\nu_{\text{OH}}$ benzoin and methyl mandelate vs dielectric constant of the solvent: (I) Cyclohexane; (II) Carbon tetrachloride; (III) Chloroform; (IV) Methylene chloride; (V) Methyl cyanide; (VI) Anisole; (VII) Diphenyl ether, (VIII) Diethyl ether; (IX) Dioxan; (X) Acetone; (XI) Acetophenone.

The interacting abilities of anisole, diphenyl ether and benzophenone are not so strong as those of dioxan, diethyl ether and acetone, but definitely stronger than that of non-oxygenated solvents as they could produce small amounts of species II and III. The magnitude of species II and III formed depends upon the strength of interaction. As the proportion of II and III determine the asymmetry of the band, the band symmetry numbers may therefore be used for assessing the relative interacting abilities. The smaller the symmetry number, the greater is the asymmetry of the band, and the greater is the proportion of species II and III. The symmetry numbers of the OH bands in the above solvents are in the order

diphenyl ether > benzophenone > anisole > acetophenone.

So the interacting abilities are in the reverse order, *viz.*,

acetophenone > anisole > benzophenone > diphenyl ether.

This is also the order of proton accepting ability, which in turn depends upon the ease with which the oxygen donates its lone pair of electrons⁷.

The marked decrease in donor ability of the oxygen of anisole compared to diethyl ether is due to the mesomeric interaction of lone pair (s) of electrons of oxygen with the phenyl ring. The donor ability of diphenyl ether is further lowered because of the lone pair(s) of electrons interacting with the additional phenyl ring.

Compared to acetophenone, benzophenone has a lower $\nu_{>C=O}$ frequency which indicates greater single bond character of carbonyl group. Therefore, it is expected to have greater electron donor ability, but in these observations, the reverse trend is noticed. It is possible to explain the low interacting ability of benzophenone on the basis of steric effects.

As in the case of benzoin, the solvent effects on methyl mandelate have been studied. The OH and $\nu_{>C=O}$ groups of methyl mandelate are involved in intramolecular hydrogen bond leading to five atom chelate^{1,8} as in benzoin. The trends in solvent shifts of ν_{OH} and $\nu_{>C=O}$ of methyl mandelate are strikingly similar to those observed in benzoin with the exception of a few differences, which are interesting and provide useful information. Shifts in ν_{OH} caused by non-oxygenated solvents are considerably larger than those observed in benzoin. This is evident from the larger slope of the straight line obtained for the plot of $\Delta\nu_{OH}$ vs dielectric constant of the solvent. This may be due to weak intramolecular hydrogen bond in methyl mandelate.

In diethyl ether and acetone solutions, the intensities of low and high frequency bands of methyl mandelate are not equal as was found in the case of benzoin. The high frequency band appeared only as a shoulder. This implies that diethyl ether and acetone solutions of methyl mandelate contain relatively larger proportion of intermolecular hydrogen bonded species (III) than in benzoin. This points out that chelation in methyl mandelate is weak and more readily cleaved by diethyl ether and acetone than in the case of benzoin. Weaker chelation in methyl mandelate is also evident from the high ν_{OH} of methyl mandelate (3540 cm^{-1}) compared to that of benzoin (3462 cm^{-1}). Weaker chelation in methyl mandelate is expected as the oxygen of the ester carbonyl is involved and is evident from these observations. The solvent effects on both benzoin and methyl mandelate reveal that the general nature of the solvent effect is the same, but the extent to which the intramolecular hydrogen bond is cleaved, varied with the same solvent.

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