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INFRARED STUDIES OF SOLVENT EFFECT: THE COMPLEXING OF CARBONYL GROUPS WITH PHENYL METHYL CARBINOL

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The self association of phenyl methyl carbinol (PMC) in carbon tetrachloride has been studied at 25°C using infrared spectroscopy and the concentration dependence of hydroxyl stretching frequency was accounted for with an association constant. A hydrogen bonded frequency shift has been observed. The influence of the carbinol hydroxyl on the carbonyl vibrations of a few representative carbonyl compounds were investigated. The integrated intensities and dipolemoment derivatives of the OH and CO bands were calculated. The formation constants for the various systems were determined and suitable structural explanations were sought for the systems studied. It is also noted that the self association is a stronger interaction than the solute-solvent interaction in the case of PMC from considerations of free energy of association.

Introduction

The study of solvent induced the frequency shifts, intensity changes and other effects of the different characteristic infrared absorption bands has been of interest during the past few years [1 — 10]. Those studies lead to the classification of solvent-solute interaction under two categories. One type corresponding to the strong or specific interaction, resulting in the formation of more or less stable complexes of polar solutes with polar liquids; which is of the donor-acceptor type and has been investigated by several workers [1]. The second type are the weak or non-specific interactions between polar solutes and non-polar or weakly polar liquids, studied in particular by Bellamy and coworkers [2], who advanced the hypothesis that even solvents which are quite non-polar form weak complexes with polar solutes. These weak interactions were explained by Horak and Pliva [3] by a process known as collision complexes in the solvent-solute systems.

An extensive study of the effect of different type of solvents of strongly interacting and weakly interacting type on the carbonyl absorption bands of representative compounds of esters, ketones and aldehydes was made by Whetsel and Kagarise [4], Krishna Pillai *et al.* [5 — 9] and Ramaswamy *et al.* [10]. Their investigations confirmed the existence of 1:1

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and 1:2 complexes in the different systems. The results supported the hypothesis proposed by Bellamy *et al.* [2], that the frequency shifts are determined predominantly by specific interactions between solvents and the solute in the low concentration region.

The investigation of Barrow [11] on the variation in the frequency, the half-width and the intensities of OH stretching vibrations of hydroxylic solutes, mainly in carbon tetrachloride solution led to the conclusion that the increase in the intensity of OH band can be understood on the basis of the increase in the ionic character of OH bond. The intensity behaviour was explained on the basis of the polarisation effect of the basic solvent on the H-bond formation [12]. The intensity changes during the change of phase in the system, was explained by pulse charge cloud model by Boobyer and Orville–Thomas [13].

The dependence and occurrence of the molecular interaction and their strength can be used with advantage in solving the confirmation and configuration of the complex organic molecules. From this view point it will be of value at this stage of investigation to supply some further fundamental knowledge relating to the strength of the interactions for the conformation of the molecule. The present investigation was undertaken with a view to have a specific understanding of the effect of solvents on the carbonyl vibration of a few representative esters, ketones and aldehydes and hydroxyl stretching vibration of phenyl methyl carbinol; and the relative contributions of the bulk dielectric effects and other types of local effects. It was also of interest to study the behaviour of hydroxyl absorption intensity and other factors, since there is also intramolecular interaction between the OH and π electrons of the benzene nucleus in general in the case of alkyl phenyl carbinols. The rotational isomerism and their effect on the hydroxyl absorption were studied by Oki and Iwamura [14, 15] for a few alkyl phenyl carbinols. The present study of self association in phenyl methyl carbinol and the solvent-solute induced effects with a few representative compounds of esters, ketones and aldehydes as proton acceptors, is with a view to study the nature of specific interactions in the various systems under consideration.

Experimental

A Hilger H 800 spectrophotometer equipped with sodium chloride optics was used with a double beam operation. The cells used were the H 890 Hilger variable path length micrometer cell and 1 mm cell with sodium chloride windows. Freshly purified samples of pure solvents and solutes and carbontetrachloride were used.

Results and discussion

The free hydroxyl absorption for phenyl methyl carbinol occurs at 3625 cm^{-1} for 0.01 M of PMC in CCl_4. With the increase of concentration of PMC another band appears at 3430 cm^{-1} till the concentration is 0.1 M of PMC. Further increase in the concentration of PMC results in an assymmetry on the lower frequency side of the 3430 cm^{-1} band, and a second band appears at 3388 cm^{-1}. Any further increase in the concentration leads to the overlapping of the two bands and the resulting band is a very broad one. Thus, at low concentrations there are two bands situated at 195 cm^{-1} and 237 cm^{-1} from the free

hydroxyl band. These bands can be explained as due to the presence of "Hydrogen bond isomerism" in phenyl methyl carbinol which arises due to the superposition of two symmetric bands and connected by hydrogen bond isomerism. Such a situation is present in phenol-acceptor systems as indicated by Fritzsche [16]. The order of separations of the hydroxyl absorption bands of PMC is in accordance with the results expected for self association in this type of carbinols.

The value of 8.93 litres/mole for the self association constant is in accordance with the results expected and compares well with the nmr value of 7.2 litres/mole reported by Oki and Iwamura [17] for a few alkyl phenyl carbinols. The free energy determined as 1.297 Kcal/m in the case of phenyl methyl carbinol is in conformity with the values expected, since it lies between the range of 0.54 ± 0.13 Kcal/m reported by Oki and Iwamura [18] and 1.4 Kcal/m reported by Schleyer [19] in a few specific carbinols and the alcohols in general. The above value of free energy is not in agreement with the values reported for hydrogen bonding in alcohols (*viz*) either with the value of 2.3 to 7 Kcal/mole reported by Coulson [20] or with the observations of Goldman and Crisler [21] thus, explaining the presence of strong interactions between the hydroxyl and the π electrons of the phenyl ring.

The integrated intensities and dipole moment derivatives were calculated for the OH vibrations using the relations given by Freeman [22]. Using the integrated intensity values and assuming that the hydrogenic vibration is a pure stretching mode the change in bond moment on stretching was calculated using the relations,

$$\frac{d\mu}{dr} = \left(\frac{1}{m_{\mathrm{H}}} + \frac{1}{m_{\mathrm{O}}}\right)^{-1/2} \frac{d\mu}{dQ} \tag{1}$$

and

$$\frac{d\mu}{dQ} = \pm \left(\frac{3C'}{\pi} A_s\right)^{1/2} \tag{2}$$

where m_{H} and m_{O} are the masses of the hydrogen and oxygen atoms, C' is the velocity of light and A_S represents the integrated intensity of the band involved in the complex. The concentrations corresponding to the bonded hydroxyl band were determined from the peak intensities of the free and complex bands. The values are presented in Table I for a few low concentrations where resolution of the two bands was possible. The value of dipole-moment derivative obtained as 0.95 esu cm^{-1} in the present investigation is in very good agreement with the value of 1 esu cm^{-1} and 0.93 esu cm^{-1} reported by Cole *et al.* [23] in the case of a few alcohols. As seen from Table I there is also initial increase in intensity and thereafter a decrease, which is in agreement with the results obtained earlier for a few phenols and cresols [10].

The next attempt was to study the effect of carbonyl on the hydroxyl vibration of phenyl methyl carbinol. The concentration of phenyl methyl carbinol was fixed at 0.01 M where self association is not present. With the addition of ethyl benzoate (EB) and benzophenone (BP) new bands appear at 3535 cm^{-1} and 3540 cm^{-1} respectively, whose intensities increase as the acceptor concentrations are increased. The integrated intensities were

TABLE I

Integrated intensities and dipolemoment derivatives for the bonded OH vibration of PMC carbon tetrachloride

Concentration of PMC in CCl_4 (m/l)	Peak frequency cm^{-1}	A_S 10^7 $cm^2\ mole^{-1}\ sec^{-1}$	$\frac{d\mu}{dr}$ 10^{10} esu cm^{-1}
0.03		1.1670	0.7210
0.05		1.5375	0.8326
0.10	3430	1.5843	0.8521
0.15		2.1293	0.9798
0.20		2.0003	0.9492
0.15	3388	2.3546	1.0303
0.20		2.0665	0.9650

TABLE II

Integrated intensities and dipolemoment derivatives of the OH stretching vibration of phenyl methyl carbinol in ethyl benzoate

Concentration of ethyl benzoate in CCl_4 (m/l)	A_S 10^7 $cm^2\ mole^{-1}\ sec^{-1}$	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$
0	0.5307	0.4890	1.0000	1.0000
0.03	0.9992	0.6710	1.8827	1.3722
0.05	1.7377	0.8848	3.2743	1.8094
0.10	1.8404	0.9108	3.4678	1.8625
0.30	1.9705	0.9419	3.7130	1.9261
0.50	2.2719	1.0162	4.2809	2.0781
0.80	2.2027	0.9936	4.1505	2.0319

TABLE III

Integrated intensities and dipolemoment derivatives of the OH stretching vibration of phenyl methyl carbinol in benzophenone

Concentration of Benzophenone in CCl_4 (m/l)	AS 10^7 $cm^2\ mole^{-1}\ sec^{-1}$	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$
0	0.5307	0.4890	1.0000	1.0000
0.05	0.5983	0.5192	1.1274	1.0617
0.10	1.4844	0.8176	2.7970	1.6719
0.15	1.6547	0.8636	3.1179	1.7661
0.20	1.6221	0.8551	3.0565	1.7487
0.30	1.6173	0.8542	3.0475	1.7468

calculated as suggested earlier [19] and the dipolemoment derivatives were calculated using the equations (1) and (2). They are presented in Tables II and III.

The frequency separations of the bonded hydroxyl and the free hydroxyl bands obtained as 90 cm^{-1} and 85 cm^{-1} in the case of ethyl benzoate and benzophenone respectively, gives us an insight about the nature of proton accepting capacity of the ester and the ketone. There is an initial increase in the intensity of the bonded hydroxyl band, and a slight decrease after a particular concentration. This represents the fact that the complexing is complete at that concentration at which the intensity reaches a maximum. This result is in accordance with the earlier observations [10].

The next interest was to investigate the effect of association on the bands of proton acceptors. A wide variety of typical carbonyl compounds representative of esters, ketones and aldehydes were chosen as proton acceptors and the phenyl methyl carbinol is taken as the proton donor. The usual pattern that is observed is the C=O band splits up into two or three (bands) components depending upon the nature of association with the donor.

In the case of ethyl acetate, phenyl acetate and ethyl benzoate two bands were observed even at comparatively low concentrations. In the case of ethyl methyl ketone, acetophenone and benzaldehyde at lower concentrations the original band only broadens out as indicated by the half-widths. At higher concentrations a new band appears at the frequencies separated by 15 cm^{-1}, 11 cm^{-1} and 10 cm^{-1} from the free carbonyl band. This band increases in its intensity with the increase in the donor concentration. At higher concentrations of the proton donor this band shifts to lower frequencies. The absence of a second band in these cases may be due to the fact that it is not possible to isolate the 1:1 and 1:2 complexes in these cases; because of the low frequency separation between these bands. This behaviour is explained by taking into account other environmental factors like the steric hindrances, resonance stabilisation which have an influence on the proton accepting capacity of the acceptor by changing the electron density. This is noted when comparing the results of the aromatic conjugated molecules like acetophenone, benzaldehyde with phenyl acetate and ethyl benzoate.

In the case of phenyl acetate, conjugation of the aromatic ring with the presence of the oxygen atom may be the reason for the high value of C=O frequency and its high hydrogen bonding ability. If the phenyl group is directly linked to the proton accepting atom, the unshared electron pair of the acceptor atom takes part in conjugation with the π electrons of the benzene ring. This will reduce the electron density at the acceptor atom. This may be the result for the weakening of the hydrogen bonding ability in acetophenone and benzaldehyde. The frequencies of carbonyl stretch absorption bands in CCl_4 and those of 1:1 and 1:2 complexes along with the frequency shifts associated with them for the various systems under study are given in Table IV.

The integrated intensities and the changes in dipolemoment for the carbonyl vibration of the various systems were calculated as described previously in the case of OH vibration. To facilitate calculations, the carbonyl vibration is assumed to be a pure stretching mode. The calculated values of the integrated intensities and dipolemoment derivatives for a few typical systems are presented Tables V to VIII.

TABLE IV

Frequencies and formation constants of carbonyl vibrations in different systems

Systems	Vibrational frequency of pure $C=0$ in cm^{-1}	Frequency of the complex band (cm^{-1})		Frequency separation (cm^{-1})		Formation constant of 1 : 1 complex (l/m)
		1 : 1	1 : 2	1 : 1	1 : 2	
Ethyl acetate + PMC	1741	1729	1722	12	7	4.03
Phenyl acetate + PMC	1768	1752	1742	16	10	2.70
Ethyl benzoate + PMC	1730	1717	1700	13	17	2.25
Ethyl methyl ketone + PMC	1719	—	1704	—	15	2.00
Acetophenone + PMC	1690	—	1679	—	11	2.20
Benzaldehyde + PMC	1708	—	1698	—	10	1.55

TABLE V

Integrated intensities and dipolemoment derivatives of the carbonyl stretching vibration of phenyl acetate in phenyl methyl carbinol

Concentration of PMC (m/l)	A_S 10^7 $cm^2 mole^{-1}$ sec^{-1}	1 : 1 complex			1 : 2 complex			
		$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$	A_S 10_7 $cm^2 mole^{-1}$ sec^{-1}	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$
0	1.1063	1.8990	1.0000	1.0000				
0.08	2.0223	2.5676	1.8279	1.3521				
0.10	2.4889	2.8471	2.2497	1.4992				
0.30	2.5856	2.9047	2.3371	1.5295				
0.50	2.6473	2.9369	2.3929	1.5465	2.4730	2.8405	2.2354	1.4958
0.80	2.7043	2.9697	2.4444	1.5638	2.5448	2.8794	2.3003	1.5163
1.50	3.1641	3.2128	2.8600	1.6918	3.4017	3.3293	3.0748	1.7532

The spectra of the various complexes were resolved by the methods of Whetsel and Kagarise [4] and Ramaswamy *et al.* [10].

The dipolemoment derivatives for 1:1 complex is found to increase with the increase of donor concentration. Further increase in the donor concentration after a particular value, leads to slight decrease in intensity and dipolemoment derivatives. An interaction of the donor molecules with the 1:1 complex may be postulated to account for this slight decrease. The intensities and dipolemoment derivatives of 1:2 complex also shows an increase with the further increase in the donor concentration. These observations are quite consistent with the earlier results [10].

The following possible structure may be proposed:

a) when one molecule of PMC is directly attached to the C=0 group, which would account for the 1:1 complex and a large frequency shift.

b) When a second molecule of PMC also gets directly attached to the carbonyl group, 1:2 complex will also be observed with a large frequency shift.

TABLE VI

Integrated intensities and dipolemoment derivatives of the carbonyl stretching vibration of ethyl acetate in phenyl methyl carbinol

Concentration of PMC (m/l)	1 : 1 complex				1 : 2 complex			
	A_S 10^7 $cm^2 mole^{-1} sec^{-1}$	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$	A_S 10^7 $cm^2 mole^{-1} sec^{-1}$	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$
0	0.8947	1.7081	1.0000	1.0000				
0.3	2.4812	2.8439	2.7732	1.6649	1.9216	2.5028	2.1477	1.4652
0.5	2.5404	2.8770	2.8394	1.6846	2.2623	2.7155	2.5285	1.5897
0.8	2.5853	2.9030	2.8896	1.6995	2.4377	2.8189	2.7246	1.6503
1.0	2.7130	2.9738	3.0323	1.7410	2.5753	2.8974	2.8784	1.6962
1.5	2.9810	3.0910	3.2759	1.8096	2.6041	2.9106	2.9135	1.7057
1.8	2.6366	2.9316	2.9469	1.7163	2.7660	3.0027	3.0915	1.7579

TABLE VII

Integrated intensities and dipolemoment derivatives of carbonyl stretching vibration of ethyl methyl ketone and acetophenone in phenyl methyl carbinol

Concentration of PCM in CCl_4 (m/l)	Ethyl methyl ketone				Acetophenone			
	A_S 10^7 $cm^2 mole^{-1} sec^{-1}$	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$	A_S 10^7 $cm^2 mole^{-1} sec^{-1}$	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$
0	0.7287	1.5412	1.0000	1.0000	1.1473	1.9339	1.0000	1.0000
0.3	1.3924	2.1321	1.9108	1.3834	...	...	...	...
0.5	1.4725	2.1926	2.0221	1.4226	4.1027	3.6588	3.5759	1.8911
0.8	...	...	...	...	4.5197	3.8384	3.9394	1.9848
1.0	2.0004	2.5539	2.7451	1.6571	...	...	...	...
1.5	...	...	...	...	6.2301	4.5062	5.4302	2.3301

TABLE VIII

Integrated intensities and dipolemoment derivatives of carbonyl stretching vibration of benzaldehyde in phenyl methyl carbinol

Concentration of PMC in CCl_4 (m/l)	$A_S 10^7$ cm^2 $mole^{-1}$ sec^{-1}	$d\mu/dr$ 10^{10} esu cm^{-1}	A_S/A_{CCl_4}	$\frac{d\mu/dr}{\left(\frac{d\mu}{dr}\right)_{CCl_4}}$
0	1.2223	2.0179	1.0000	1.0000
0.5	2.3508	2.7680	1.9233	1.3717
0.8	2.4731	2.8392	2.0233	1.4070
1.0	2.7504	2.9957	2.2501	1.4846
1.2	3.9787	3.6021	3.2551	1.7851
1.5	4.3071	3.6964	3.5237	1.8318

c) Instead of getting itself attached to C=O group directly, the second molecule of the donor may be attached to the oxygen of PMC itself, because of the influence of the π-electrons of the benzene nucleus with the lone pair electrons of the oxygen atom or the steric factors coming into play because of the presence of alkyl groups with the phenyl ring. The frequency shifts associated with such 1:2 complex will be very small and hence unresolvable.

The large frequency shifts associated with the 1:1 and 1:2 complexes in the case of phenyl acetate, ethyl acetate and ethyl benzoate favour the structure in which two molecules of the donor are directly attached to the carbonyl group. The position in which donor hydrogen aligns itself with one of the two lone pairs of electrons of the oxygen atom of the acceptor to form a bond like, O—H...O=C to indicate that the H bond joins together two bonds is the most favourable for the maximum interaction to occur between the lone pair atomic dipole and the O—H bond thus forming the 1:1 complex. The systems in which low frequency shifts are observed for the 1:2 complex and in which 1:1 and 1:2 complexes are unresolvable can be explained on the basis of the structure (C) explained above.

The changes in dipolemoment of the complex can be explained by contending the vibrations of the lone pair of electrons in consonance with the vibrations of the O—H bond. In the case of carbonyl band intensity, this is due to the fact that the C=O induces a moment in OH bond which leads to the increase in the observed intensity of the carbonyl stretch. The differences in the polarisability which is responsible for the induced dipole moment. The lowering of carbonyl frequency with the increase of OH concentration is due to the weakening of the C=O bond strength. When all the lone pairs of the carbonyl group have been bonded there will not be any further change in the intensity.

The above observations support the presence of specific interactions in the form of 1:1 and 1:2 complexes in the low concentration regions. Two types of classification of the carbonyl compounds have been made according to the nature of specific interactions present. One type corresponds to those in which the interactions are high and in which the 1:1 and 1:2 complexes are well resolved. These are the types in which there is direct linking between donor and acceptor groups. The second types are those in which the 1:1 and 1:2 are not well resolved, which favour the structure proposed by Whetsel and Kagarise [4], in which the donor molecules form "the associated species" and they combine with the C=O group. The quantitative explanation for the variations in the intensities and dipole moment derivatives can be given on the basis of the pulse charge cloud model of Boobyer and Orville-Thomas [13].

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