The Effect of Solvent on Infrared Absorption Bands of Halogenated Hydrocarbon Molecules

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The intensities of infrared absorption bands have hitherto been measured with two main objects, namely for qualitative and quantitative analyses and for elucidating structural problems, and most of the measurements have been made in solution because the measurements in gaseous state are often difficult. Nevertheless the effects of solvent on infrared absorption bands have scarcely been studied except for the particular case where the hydrogen bond is concerned, and the intensity of the band, especially the area intensity of the band, has often been assumed to be independent of the solvent used. Recently Whiffen[1] has measured an infrared absorption band of chloroform near 760 cm^{-1} and has concluded that the area of the band is approximately independent of solvents although the peak height and the width at half height change considerably with them.

The present work was undertaken to see the effects of solvents on some degenerate and non-degenerate infrared absorption bands of polar and non-polar halogenated hydrocarbon molecules. In particular it seems to be of interest to know whether or not the band area is kept constant for the variety of solvents.

Experimental

Absorption measurements were made for the bands of carbon tetrabromide[2], *cis*-1,4-dibromocyclohexane and *trans*-1,4-dichlorocyclohexane. Following Bartal's method[3] carbon tetrabromide was prepared from acetone and bromine. (m.p. 93°C). The absorption band measured for this compound is the triply degenerate one, the peak frequency of which is about 670 cm^{-1}.

cis-1,4-Dibromocyclohexane[4] was synthesized from chinit and hydrobromic acid by the method used by Rothstein[5] and was separated from *trans*-1,4-dibromocyclohexane by fractional crystalizations using petroleum ether and methanol as solvents, repeatedly one after another. (m.p. 49°C)[6]. The purity was certified by the infrared inspection. The solvent effect was measured for the nine strong bands in the region from 7 to 23μ.

trans-1,4-Dichlorocyclohexane was made from chinit and hydrochloric acid by Rothstein's method[5]. (m.p. 102°C). This compound has two isomeric forms, the abundance ratio of which changes with solvents[7,8]. The solvent effects were, therefore, observed only for the changes of band widths and peak frequencies. The peak frequencies were measured for the bands in the region from 7 to 23μ, but the half intensity widths were measured only for the bands near 475, 565, 760 and 785 cm^{-1}, because the bands of two isomers above 800 cm^{-1} appear in close pairs and the band widths, therefore, cannot be measured accurately.

The spectral data were obtained with Perkin-Elmer Model 112 spectrometer with KBr prism for the region from 14 to 23μ and with NaCl prism for the region from 7 to 14μ. The thicknesses of cells used were 0.102 and 0.103 mm,

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[1] D.H. Whiffen, *Trans, Faraday Soc.*, **49**, 878 (1953).

[2] Since one of the two infrared active bands of carbon tetrachloride lies in the region where KBr is not transparent and the other appears near 780 cm^{-1} as doublet (Fermi resonance), this compound is not suitable to use for the present purpose.

[3] A. Bartal, *Chem. Zt.*, **29**, 377 (1905).

[4] Detailed report on this compound by Kozima and Yoshino will be soon published in other place.

[5] M.B. Rothstein, *Ann. chim.*, **14**, 461 (1930).

[6] m.p. in literatures is 48°C or lower. See, for example, 5) or E. L. Bennett and C. Niemann, *J. Am. Chem. Soc.*, **74**, 5076 (1952).

[7] K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).

[8] T. Yoshino, *J. Chem. Soc. Japan*, **75**, 592 (1954).

which were measured with the interference method. The slit width employed was such that the spectral slit width was nearly equal to, or narrower than half of the half intensity width and kept constant for the variety of solvents. The spectral slit width S was calculated9) by the following formula, which was obtained by the simple modification of the formula10) for single pass spectrometer,

$$S=\tilde{\nu}^2\frac{[1-n^2\sin^2(\alpha/2)]^{1/2}}{8\sin(\alpha/2)\,(dn/d\lambda)}\frac{s}{f}+\frac{\tilde{\nu}}{4l\,(dn/d\lambda)}$$

where $\tilde{\nu}$ is frequency in cm^{-1}, n is index of refraction at frequency $\tilde{\nu}$, α is prism apex angle, $dn/d\lambda$ is dispersion of prism material, and s, f and l are the slit width, the focal length and the length of prism base in cm. unit respectively.

The absorption curves of solvent and solution were recorded using the same cell, and constancy of recording condition was checked before and after each measurement using the reference cell filled with solvent. Errors due to stray light and non linearity of the amplifier were negligible.

Results and Discussions

The abbreviations used in this paper are as follows:

$\tilde{\nu}_{max}$ = frequency at the peak in cm^{-1}.

ε_{max} = apparent peak intensity in $10^5\ cm^{-1}\ mol.^{-1}$. The base of logarithm is 10.

ε_{max} (corr.) = peak intensity in $10^5\ cm^{-1}\ mol.^{-1}$, with Ramsay's slit-width correction11), assuming Lorentzian curve:

$$a=B/[b^2+(\tilde{\nu}-\tilde{\nu}_0)^2].$$

b' = frequency interval in cm^{-1} between the band center and the half height position on long wave length side.

b'' = the same one on the short wave length side.

$2b=b'+b''$.

$2b$ (corr.) = $2b$ value with slit-width correction.

$\int\varepsilon d\nu$ = band area in $10^{16}\ cm^2\ sec.^{-1}\ mol.^{-1}$.

$\log I_0/I$ = absorbance at the peak used to correct ε_{max} and b.

range = integration range in cm^{-1}. Except for the carbon tetrabromide band, the integration range is taken so that the absorption peak lies in its center.

First of all, let us consider the band of carbon tetrabromide. The results are shown in Table I for the various solvents used. The frequencies of the absorption peak in dioxane and in ethyl acetate are higher than those in n-heptane and in carbon tetrachloride. These results do not agree with Whiffen's results for chloroform band, which show that the peak frequency becomes highest in n-heptane and lowest in dioxane and in general is higher in non-polar solvents and lower in polar solvents.

The apparent half intensity width of the carbon tetrabromide band changes very much with solvents and is smaller in n-heptane and in carbon tetrachloride and larger in dioxane and ethyl acetate in accordance with the results of the chloroform band. We see, therefore, that in the carbon tetrabromide band the wider absorption is not accompanied with lower value of peak frequency as was mentioned in reference to the chloroform band.

The large half intensity width is accompanied by the low absorption peak, as is shown in Table I, so that the band areas in various solutions are brought near a definite value, but the differences of the areas are greater than the experimental error. The band area is larger in the solvent which lowers the peak frequency.

TABLE I

Solvent	$\tilde{\nu}_{max}$	ε_{max}	b'	b''	$\int\varepsilon d\nu$	$\log I_0/I$
dioxane	674.8	2.87	14.1	9.3	22.4	0.39
ethyl acetate	672.9	3.05	11.4	13.1	24.1	0.39
n-heptane	672.5	9.15	4.4	3.7	23.8	0.47
carbon tetrachloride	671.8	7.39	5.5	4.8	27.0	0.38

$2S=8.3$

The values of area intensities in Table I were integrated over the frequency ranges from $\tilde{\nu}_{max}-3b'$ to $\tilde{\nu}_{max}+3b''$ cm^{-1}. The band shapes are not symmetric, namely b' is not equal to b''. The solvent changes not only b' and b'' but also the ratio of them. The absorption curve, especially on the high frequency side of the peak, does not fit the Lorentzian curve even if the slit-width correction is made. The absorbance at $\tilde{\nu}_{max}-3b'$ and at $\tilde{\nu}_{max}+3b''$ are about 1/20 and 1/40 of that at the peak respectively and are smaller than those obtained from the Lorentzian

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9) The values of n and $dn/d\lambda$ were takec from: C. Schäffer and F. Matossi, "Das Ultraroc Spektrum", Julius Springer, Berlin (for NaCl) and R. E. Stephens, E. K. Plyler, W. S. Rodny and R. J. Spindler, *J. Opt. Soc. Am.*, **43**, 110 (1953) (for KBr).

10) For example, van Z. Williams, *Rev. Sci. Inst.*, **19**, 135 (1948).

11) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

curve (1/10) by use of the peak height and the b' or b'' value with slit-width corrections. Owing to rather rapid decrease of absorption on the wings outwards from the center, the sum of the areas outside of the integration range may by estimated to be about one tenth of the band area and the ratio may not vary with solvents. Therefore the values of band areas in Table I integrated over the finite regions may be used for the comparison of band areas in various solutions in place of the values of infinite integration ranges.

The results of the measurements of the bands of *cis*–1,4–dibromocyclohexane near 505, 640 and 740 cm^{-1} are given in Tables II and III. The shapes of these bands are approximately the Lorentzian form. The Lorentzian curve suitable for the region near the band center does not accurately fit the wings and has a little larger value of absorbance than that observed. The peak frequencies of these bands take lower values in benzene, dioxane and polar solvents and the lower peak frequencies are accompanied with the wider half intensity widths. These effects are in accordance with those observed for chloroform band but the changes of the band widths with solvents are not so large as those in the degenerate bands of carbon tetrabromide and chloroform.

TABLE II

Solvnet	$\tilde{\nu}_{\max}$ or $\Delta\tilde{\nu}_{\max}$	$\varepsilon_{\max}$	$\varepsilon_{\max}$ (corr.)	$2b$	$2b$ (corr.)	$\int\varepsilon d\nu$	$\log I_0/I$
n-heptane	506	0.57	0.63	6.6	5.8	1.43	0.30
cyclohexane	−0.0	0.60	0.67	6.1	5.3	1.39	0.30
carbon tetrachloride	−0.9	0.62	0.67	6.6	5.9	1.48	0.36
benzene	−3.2	0.62	0.67	7.1	6.4	1.61	0.36
chloroform	−3.2	0.56	0.59	8.2	7.6	1.58	0.32
elthyl acetate	−3.6	0.52	0.55	8.1	7.5	1.52	0.34
dioxane	−3.6	0.57	0.59	8.2	7.6	1.71	0.32
n-heptane	645	1.07	1.30	7.3	5.8	2.99	0.28
cyclohexane	−0.0	1.05	1.27	7.3	5.8	2.90	0.30
carbon tetrachloride	−1.1	1.09	1.30	7.5	6.0	3.10	0.31
chloroform	−3.5	1.11	1.25	8.6	7.3	3.18	0.31
cyclohexane	739	0.93	1.19	4.5	3.3	1.61	0.29
benzene	−2.3	0.95*	1.2 *	4.6*	3.4*	1.7 *	0.31*
dioxane	−2.7	1.01	1.24	4.8	3.7	1.88	0.36

$2S=4.7,\ 7.0,\ 4.7$, range$=23.5,\ 32.7,\ 17.7$, for the bands near 505, 640, 740 cm^{-1} respectively.
* These values are inaccurate because of the absorption of the solvent.

TABLE III

Solvent	$2S$	$\varepsilon_{\max}$	$\varepsilon_{\max}$ (corr.)	$2b$	$2b$ (corr.)	$\int\varepsilon d\nu$	$\log I_0/I$
dioxane	3.4	0.57	0.59	8.0	7.7	1.71	0.32
	4.7	0.57	0.59	8.2	7.6	1.71	0.32
	6.7	0.56	0.62	8.7	7.6	1.72	0.31
	8.7	0.52	0.61	9.5	7.6	1.70	0.28
n-heptane	3.4	0.59	0.61	6.4	6.0	1.43	0.31
	4.7	0.57	0.63	6.6	5.8	1.43	0.30
	6.7	0.51	0.61	7.2	5.7	1.39	0.27
	8.7	0.47	0.63	7.7	5.4	1.31	0.25

$2S=23.5$

For the absorption curve of dioxane solution, Lorentzian form is a good approximation. Assuming the Lorentzian curve with $B/b^2=0.59$ and $2b=7.6$, the area intensity with infinite integration range is 2.12 which is 24% larger than the value in the Table.

The wings of the absorption band spread over very wide ranges and the area in the wings is not negligible in spite of the small absorbances in the wingths. But as it is hard to obtain the area in the wings with accuracy, the values in Tables II and III were integrated over the definite spectral intervals of about four times of the half intensity widths. The band areas shown in the Table increase with solvents which lower the peak frequency and broaden the band. The area outside of the integration range and its ratio to the integrated area of the broadened band are larger than those of the narrowed band.

Then the increment of the band areas above mentioned is not diminished even if integrated over the infinite range. As the areas outsied of the integration ranges in various solutions are different from each other only by a small percent of the integrated area, the increment of band area integrated over infinite range is approximately the same as that shown in Table II and might not exceed 30% for the 505 cm^{-1} band in which the increment is largest.

The transmission measured is the average of the transmissions for the interval of the slit width. Therefore the band area measured, particularly when the integration range is limited, might be smaller than that with infinitely small slit width and this diminution might depend upon the ratio of the band width to the spectral slit width. The area of the band near 505 cm^{-1} was measured with various slit widths for the *n*-heptane (which narrows the band width) and dioxane (which broadens the band width) solutions, but the band areas were found to be independent of slit width as shown in Table III so far as the half intensity width is smaller than twice the spectral slit width. The change in the ratio of the band width to the slit width, therefore, does not make any contribution to the change of the band area with solvents.

The decrease of the band areas in *n*-heptane and cyclohexane is not due to the change of molecules from one form to the other. The reason for this is as follows. As all the bands below 800 cm^{-1} decrease their intensities in the same manner in these solvents, they must belong to one form which is much more populated than the other. Owing to the change of molecules which causes the decrease of the band areas observed, the increase of the band areas of less populated form, if it exists, should be remarkable so far as any of the bands is not covered by the absorption of the more populated form or has appreciable absorbance. But none of the bands which show such a remarkable increase of band area in *n*-heptane or in cyclohexane solution was found in the region from 7 to 23μ. Thus we can see that the change of area intensity without change of molecules takes place for the bands of this compound. Such a change of band area has also been observed for the C=O stretching bands of ketones[12] in chloroform and carbon tetrachloride in accordance with the present results.

In carbon tetrachloride solution the frequency, width and area of the absorption band take intermediate values of those in polar and non-polar solvents.

The shapes of the bands above 800 cm^{-1} are also nearly Loretzian form and the band widths change with solvents as the bands below 800 cm^{-1}. But some of the solvent effects on the higher frequency bands are different from that described before. The peak frequencies of these bands, as shown in Table IV, do not change with solvents and the change of band areas is not

TABLE IV

$\tilde{\nu}_{\max}$	$2S$	Range	Solvent	$\varepsilon_{\max}$	$2b$	$\int \varepsilon d\nu$
872	3.7	26.3	carbon tetrachloride	1.16	5.3	2.5
			benzene	1.06	5.5	2.4
			chloroform	1.23	5.4	2.7
991	4.2	21.3	cyclohexane	1.68	4.0	2.8
			carbon tetrachloride	1.74	3.9	2.8
			chloroform	1.80	4.1	3.2
			dioxane	1.55	4.5	2.8
1162	5.1	32.5	cyclohexane	0.78	6.4	2.1
			carbon tetrachloride	0.78	6.5	2.1
1206	5.2	30.3	cyclohexane	1.14	7.9	3.5
			carbon tetrachloride	1.12	8.3	3.5
			benzene	1.07	9.7	3.7
1259	5.4	40.6	carbon tetrachloride	1.65	7.1	4.8
			benzene	1.71	7.7	5.3
1341	6.1	22.1	cyclohexane	0.91*	5.9*	2.2*
			carbon tetrachloride	1.09	5.4	2.4
			benzene	0.99	5.5	2.3
			chloroform	1.11	5.7	2.5

* These values are inaccurate because of the absorption of the solvent.

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[12] G. M. Barrow, *J. Chem Phys.*, **21**, 2008 (1953).

TABLE V

Solvent	$2S$	ν_{max} or $\Delta\nu_{max}$	$2b$	$2b$ (corr.)	$\log I_0/I$
cyclohexane		476	5.2	3.8	0.24
carbon tetrachloride	5.6	−0.8	5.2	3.9	0.41
benzene		−2.0	5.4	4.1	0.35
cyclohexane		566	7.3	6.7	0.48
carbon tetrachloride	4.5	−2.2	7.8	7.3	0.81
benzene		−4.5	8.0	7.5	0.45
cyclohexane		759	3.5	2.9	0.64
benzene	3.3	−3.2	4.1	3.5	0.46
dioxane		−4.2	5.0	4.4	0.43
cyclohexane		786	4.5	3.8	0.40
benzene	3.7	−3.8	5.6	5.1	0.47
dioxane		−4.9	6.0	5.5	0.55

the same for all these six bands nor analogous to that mentioned to the lower frequency bands.

For the bands of *trans*–1,4–dichlorocyclohexane, the solvent effect on the peak frequencies and the widths shown in Table V is the same as that described for the bands of *cis*–1,4–dibromocyclohexane. The peak frequencies of the bands above 800 cm^{-1} which are not given in the Table do not change appreciably with such solvents as cyclohexane, carbon tetrachloride, chloroform and benzene.

So far as the molecules discussed are concerned, the frequency lowering with solvents takes place only for the bands which are related intimately to the stretching and deformation of carbon-halogen bonds. These changes may be due to the perturbation of the solute molecules caused by the action of solvent on the carbon-halogen bonds[13].

We have seen above that the integrated intensity of an absorption band of halogenated hydrocarbon molecules is not kept constant for the variety of solvents and this intensity change is remarkable in low frequency bands. Chako's theory[14] fails to explain this increase of band area, so far as the index of refraction of pure solvent in visible light is used. In this respect it is of interest that the solvent which lowers the peak frequency, broadens the band width and increases the band area is the one which stabilizes the polar form of rotational isomers[15].

In the degenerate bands mentioned above, large changes of band widths and peak heights took place. This remarkable feature might be due to the splitting of degeneracy. The frequency change in the carbon tetrabromide band is different from those in the bands of chloroform and cyclohexane derivatives. This peculiarity of carbon tetrabromide seems to be due to the spherically symmetric form of the molecule and seems to coincide with the action of carbon tetrachloride as non-polar solvents like *n*-heptane and cyclohexane as was seen in the present results.

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[13] Detailed report on the studies of the solvent-solute interaction using mixed solvents will be published in near future.

[14] N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

[15] The elongated form of *trans*-1,4-dichlorocyclohexane corresponds to the polar form in regard to the solvent effect on the abundance ratio. The correspondence was elucidated in 8).