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INFRARED SPECTRA OF FLUORAL, CHLORAL AND BROMAL HYDRATES

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Infrared spectra of fluoral, chloral and bromal hydrates*

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Abstract—The infrared spectra of fluoral, chloral and bromal hydrates have been investigated. There are two $\nu(\text{OH})$ bands in the dilute-solution spectra and these are attributed to free and intramolecularly bonded OH groups; there is some evidence that bonding may be to halogen but the matter is uncertain. There is evidence that previous suggestions that the stability of the hydrates is due to interactions of the kind $\text{Cl} \cdots \text{H}-\text{O}$ is incorrect. The CH bending frequencies in the solids have been assigned.

Introduction

THE infrared spectrum of polychloral [1] has two bands in the region $1500\text{--}1300\text{ cm}^{-1}$ which are due to CH bending motions. It was not known whether or not they are due to the similar motions of two or more CH groups coupled, the other motions of the CH group giving bands in a lower frequency range. The infrared spectrum of chloral hydrate should give useful information on this point because its CH group is in a similar environment to that in polychloral, i.e. the carbon atoms are attached to similar atoms. We have therefore examined the spectra of fluoral, chloral and bromal hydrates and their methylated and deuterated derivatives. There are a number of other interesting features in the spectra, and these are also reported.

The dissociation equilibrium of aliphatic aldehyde hydrates, $\text{RCH}(\text{OH})_2 \rightleftharpoons \text{RCHO} + \text{H}_2\text{O}$, in inert solvents strongly favours free aldehyde and water under normal conditions. Hydrates of halogen-substituted aldehydes dissociate much less, and their stability increases with increasing number of halogen atoms in the molecule [2]. Hydrates of fluoral, chloral and bromal, $\text{CX}_3\text{CH}(\text{OH})_2$ ($\text{X} = \text{F}, \text{Cl}$ and Br , respectively), can be isolated pure and their stability increases with increasing electronegativity of the halogen atom. The stability of chloral hydrate has been said to be due to the interaction via the hydrogen atom between the OH groups and the adjacent CCl_3 group [3, 4]. KONDO and NITTA [5] have determined the crystal structure of chloral hydrate by X-ray diffraction, and they have suggested that, contrary to expectation if the stability is in large part due to $\text{OH}-\text{CCl}_3$ interaction, there are intermolecular rather than intramolecular hydrogen bonds in the crystal. Our spectra give some information on this point.

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[1] A. NOVAK and E. WHALLEY, *Trans. Faraday Soc.* **55**, 1490 (1959).

[2] P. FEDERLIN, *Compt. rend.* **235**, 44 (1952).

[3] M. M. DAVIES, *Trans. Faraday Soc.* **36**, 333, 1114 (1940).

[4] P. BARGHEWITZ, *Compt. rend.* **232**, 1750 (1951).

[5] S. KONDO and I. NITTA, *X-Sen* **6**, 53 (1950).

Spectra have been published previously as follows. The Raman spectrum of chloral hydrate in water solution has been recorded by FONTEYNE [6] and those of crystalline chloral and bromal hydrates by SEEWAN-ALBERT [7]. The infrared spectrum of liquid fluoral hydrate has been published by HUSTED and ALBRECHT [8] and that of chloral hydrate by DAVIES [3] and most recently by BELLAMY *et al.* [9]

Experimental

Chloral hydrate, chloral hydrate- d_2 and chloral monomethylalcoholate [$\text{CCl}_3\text{CH}(\text{OH})\text{OCH}_3$] were prepared by treating freshly distilled chloral (Eastman Kodak White Label) with equivalent amounts of water, heavy water and methanol, respectively. Bromal hydrate and its deuterated and methylated derivatives were prepared from freshly distilled bromal (Eastman Kodak White Label) by the same methods. The substances were dried in a stream of dry air over phosphorus pentoxide. Fluoral hydrate was obtained from Dr. L. C. LEITCH of the Pure Chemistry Division, and was distilled through a column of Drierite before use.

Fluoral hydrate was investigated as the pure liquid, in solution in CCl_4 at various concentrations and in the vapour state. Chloral and bromal hydrates and their derivatives were studied in the solid state as mulls in Nujol and hexachlorobutadiene and in solution in CCl_4 at various concentrations. Chloral hydrate was also studied in CS_2 . The spectra were recorded between 4000 and 700 cm^{-1} on a Perkin-Elmer model 21 infrared spectrophotometer using CaF_2 and NaCl prisms and between 700 and 300 cm^{-1} using a Beckman IR-4 instrument with a CsBr prism. The wave-numbers of sharp bands in the high-frequency region were measured to an accuracy of $\pm 2\text{ cm}^{-1}$. Water vapour was used for calibration, and solutions of methanol and isopropanol in CCl_4 were recorded for comparison.

Results and discussion

1. The 3- μ region

All the hydrates have one or more broad bands in the 3- μ region (Fig. 1 and Table 1), as follows: liquid fluoral hydrate, 3360 cm^{-1} ; solid chloral hydrate, 3360 cm^{-1} and a shoulder at 3280 cm^{-1} ; solid bromal hydrate, 3440, 3350 and 3190 cm^{-1} . None is present in dilute solutions and so they are due to intermolecularly bonded OH groups. In carbon tetrachloride, each hydrate has three bands. One, at about 3410 cm^{-1} , is rather broad, diminishes in relative intensity on dilution and disappears at concentrations lower than about 0.01 M. It can probably be attributed to associated molecules, similar to the associated molecules of alcohols [10]. The other two bands, between 3620 and 3500 cm^{-1} , are as sharp as those of free OH groups of alcohols and phenols, and remained unchanged on dilution to 0.005 M and lower. Chloral hydrate gives similar, slightly shifted bands in carbon disulphide solution. DAVIES [3] had found only one $\nu(\text{OH})$ band,

[6] R. FONTEYNE, *Natuurw. Tijdschr.* **24**, 69 (1942).

[7] H. SEEWAN-ALBERT, *Acta Phys. Austriaca* **1**, 346 (1948).

[8] D. R. HUSTED and A. H. ALBRECHT, *J. Am. Chem. Soc.* **74**, 5422 (1952).

[9] D. M. W. ANDERSON, L. J. BELLAMY and R. L. WILLIAMS, *Spectrochim. Acta* **12**, 233 (1958).

[10] R. N. JONES and C. SANDORFY, *Technique of Organic Chemistry* (Edited by A. WEISSBERGER) Vol. IX, p. 417. Interscience, New York (1956).

3564 cm^{-1} , in the solution spectrum of chloral hydrate, but observed that it was broader than that of a monohydric alcohol under the same conditions.

The cause of the two dilute-solution $\nu(\text{OH})$ bands is of some interest. The splitting seems too big for coupling between the motions of the two OH groups to be the cause; in addition, fluoral hydrate vapour gives only one band at 3616 cm^{-1} .

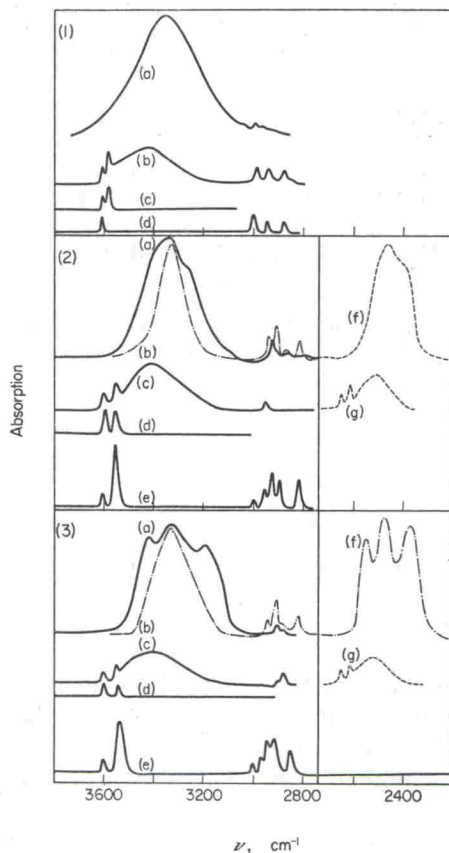


Fig. 1. The 3800 to 2200 cm^{-1} region of the infrared spectra of fluoral, chloral and bromal hydrates and derivatives.

- (1) Fluoral hydrate: (a) pure liquid; (b) and (c) 0.05 M and 0.01 M solutions; (d) vapour.
 (2) Chloral hydrate: (a) solid; (c) and (d) 0.05 M and 0.01 M solutions. Chloral monomethylalcoholate (b) solid; (e) 0.04 M solution. Deuterated chloral hydrate (f) solid; (g) solution.
 (3) Bromal hydrate: (a) solid; (c) and (d) solutions. Bromal monomethylalcoholate (b) solid; (e) solution. Deuterated bromal hydrate (f) solid; (g) solution. All solid substances are mulls in hexachlorobutadiene. All solutions are in carbon tetrachloride.

One band is not due to water, which may be formed by dissociation of the hydrate, because the water band occurs at 3708 cm^{-1} [11] in CCl_4 and it would hardly be observable in 1-mm cells, and also fluoral hydrate hardly dissociates. It is very unlikely to be caused by Fermi resonance; its occurrence in fluoral, chloral and bromal hydrates, and in deuterated chloral and bromal hydrates, demands too

[11] P. SAUMAGNE and M. L. JOSIEN, *Bull. soc. chim. France* 813 (1958).

Table 1. OH stretching frequencies of fluoral, chloral and bromal hydrates and derivatives

Compound	Vapour	Solution in carbon tetrachloride					Solid
		Free	Bonded	Free-bonded $\Delta\nu$	Intensity ratio free-bonded	Associated	
Fluoral hydrate	3616	3613	3578	35	1 : 1.5	3420	3360 (liquid)
Chloral hydrate		3605	3558	47	1 : 0.9	3410	3360, 3280 (solution in CS ₂)
		3578	3550	28	1 : 1.1		
Bromal hydrate		3602	3545	57	1 : 0.9	3410	3440, 3350, 3190
Chloral hydrate- <i>d</i> ₂		2651	2620	31		2510	2475, 2390
Bromal hydrate- <i>d</i> ₂		2650	2612	38		2530	2540, 2465, 2360
Chloral mono-methylalcoholate		3605	3558	47	1 : 6	3450	3350
Bromal mono-methylalcoholate		3602	3545	57	1 : 6	3450	3340

much coincidence. It seems likely, therefore, that the two bands are due to two OH groups in different environments, the higher of which is relatively free and the lower relatively bonded, either to halogen or to oxygen, in a similar manner to the dihydric alcohols [12]. It is difficult to determine whether the bonding is to halogen or to oxygen. If it is to oxygen a four-membered ring is formed, and if to halogen, a five-membered. Thus, though an O—H...O bond is stronger in its strongest orientation than an O—H...halogen bond, the O—H...O bond in the hydrates would be more bent and so presumably reduced in strength more than the O—H...halogen bond. The fact that the difference in frequency between the free and bonded OH increases in the series fluoral, chloral, bromal hydrates, which is the same order as the increasing size of the halogen and so of increasing overlap with the hydrogen, is an indication that a bond to halogen might occur, but the matter cannot be considered as settled. The positions of the $\nu(\text{OH})$ bands are rather similar to those for the *o*-halophenols [13], where hydrogen-bonding to halogen seems to be well established. As we have already mentioned, fluoral hydrate vapour has only one $\nu(\text{OH})$ band. The reason for the difference between solution and vapour is not known. A possible explanation is that the two bands

[12] L. P. KUHN, *J. Am. Chem. Soc.* **74**, 2492 (1952).[13] A. W. BAKER, *J. Am. Chem. Soc.* **80**, 3598 (1958).

are very close in the vapour, but have very different shifts due to solvent. However, it seems unlikely that such different relative shifts, 0.8×10^{-3} and 9.7×10^{-3} , would occur with two bands whose intensities are so nearly the same. It is more likely that the solvent affects the equilibrium between bonded and non-bonded forms.

Chloral and bromal methylalcoholates $[\text{CX}_3\text{CH}(\text{OH})\text{OCH}_3]$ have three $\nu(\text{OH})$

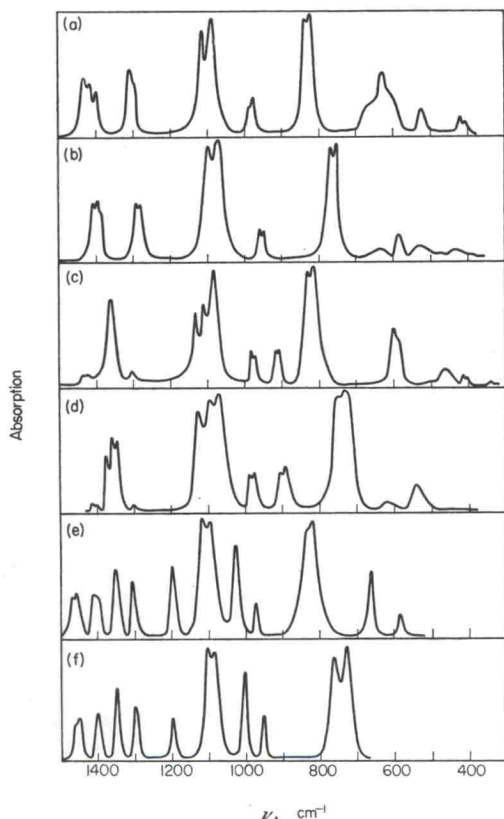


Fig. 2. The 1500 to 400 cm^{-1} region of the infrared spectra of solid chloral and bromal hydrates and derivatives; mulls in Nujol and hexachlorobutadiene: (a) chloral hydrate; (b) bromal hydrate; (c) chloral hydrate- d_2 ; (d) bromal hydrate- d_2 ; (e) chloral monomethylalcoholate; (f) bromal monomethylalcoholate.

bands in carbon tetrachloride solution. The associated band of chloral methylalcoholate at about 3450 cm^{-1} disappears at about a four-times-higher concentration ($\sim 0.04 \text{ M}$) than that of the hydrate ($\sim 0.01 \text{ M}$). The free and bonded $\nu(\text{OH})$ bands are present, but with smaller intensity ratios of free to bonded than in the hydrates. Dissociation to aldehyde and methanol spoiled an attempt to measure the temperature coefficient of the intensity ratio.

It has been suggested [3, 4] that the stability of these hydrates is due to the formation of intramolecular hydrogen bonds $\text{O}-\text{H} \cdots \text{X}$. The fact that the order of increasing stability of the hydrates, bromal, chloral, fluoral, is the reverse of the order of increasing hydrogen-bond strength as measured by the difference between the bonded and non-bonded frequencies (Table 1), is evidence against this hypothesis.

2. *Region below 1500 cm⁻¹*

We wished to know, in connexion with our work on polychloral [1], the number of CH deformation frequencies in the range 1500–1300 cm⁻¹ in the hydrates. Fluoral hydrate is not well suited to this because of the interference by strong $\nu(\text{CF})$ bands. The spectra of solid chloral and bromal hydrates and their O-deuterated and monomethylated derivatives are shown in Fig. 2, and the wave-numbers and

Table 2. Wave-numbers and relative intensities of the absorption bands of chloral and bromal hydrates and derivatives (1500 to 400 cm⁻¹ region)

Chloral hydrate	Bromal hydrate	Chloral hydrate- d_2	Bromal hydrate- d_2	Chloral monomethyl-alcoholate	Bromal monomethyl-alcoholate	Approximate description
				1462 1455 (s)	1460 1450 (s)	$\delta_a(\text{CH}_3)$
1427 1412 (s) 1392	1408 1395 (s) 1385			1407 1390 (s)	1403 (s)	$\delta(\text{CH} + \text{OH})$
		1365 1360 (s)	1368 1350 1343 (s)	1358 (s)	1352 (s)	$\delta_s(\text{CH}_3)$ $\delta(\text{CH})$
1305 1295 (s)	1290 1277 (s)			1302 (s) 1198 (m)	1295 (s) 1195 (m)	$\delta(\text{CH} + \text{OH})$ $\gamma_r(\text{CH}_3)$
		1134 (s)	1130 (s)			
1110 (vs)	1090 (vs)	1106 (s)	1085 (vs)	1115 (vs)	1102 (vs)	$\nu(\text{C—O})$
1086 (vs)	1070 (vs)	1085 (vs)	1070 (vs)	1087 (vs)	1080 (vs)	
				1025 (s)	1001 (s)	$\nu(\text{CH}_3\text{—O})$
985 975 (m)	957 946 (m)	980 965 (m)	990 975 (m)	967 (m)	955 (m)	$\delta(\text{CH})$
		912 904 (m)	905 885 (m)			$\delta(\text{OD})$
835 (vs)	761 (vs)	827 (vs)	750 (vs)	830 (vs)	760 (vs)	$\nu(\text{C—CX}_3)$
825 (vs)	750 (vs)	810 (vs)	735 (vs)	815 (vs) 662 (s)	735 (vs)	
630 (sh)	620 (w)		620 (w)			$\gamma(\text{OH})$
620 (m) 520 (m)		590 (s) 465 (m)	530 (m)	580 (m)		$\gamma(\text{OD})$
422 415 (w)	450 (w)	416 410 (w)				

relative intensities are given in Table 2. Chloral and bromal hydrates have two bands in the range $1500\text{--}1300\text{ cm}^{-1}$, while the O-deuterated compounds have only one band at about 1360 cm^{-1} ; some of the bands are split into two or three components. The $1500\text{--}1300\text{ cm}^{-1}$ bands of chloral hydrate have been assigned [9] to coupled CH and OH deformation modes; the corresponding bands of bromal hydrate are probably due to similar motions. The splitting of the bands, which is more pronounced with the CH and OH bands than with other bands, may be due either to non-equivalently bonded OH groups [9], or to crystal effects, there being four molecules of chloral hydrate in the unit cell [5]. The one band in this region in the O-deuterated hydrates must be a CH deformation mode; there is therefore only one $\delta(\text{CH})$ band in the region $1500\text{--}1300\text{ cm}^{-1}$, and the second must be below. Its assignment is uncertain. A candidate is a band at about 970 cm^{-1} , which is split into two components in the crystal; the splitting is probably due to crystal effects because only one band occurs in the solution spectrum. In support of this assignment, hexachloroacetone hydrate, $(\text{CCl}_3)_2\text{C}(\text{OH})_2$, which does not contain a CH group, has no band between 1000 and 900 cm^{-1} [9].

There is a broad shoulder at about 630 cm^{-1} in the spectrum of chloral hydrate, which shifts to 460 cm^{-1} on deuteration, and it is attributed to an OH deformation mode. This band is very similar to the $\gamma(\text{OH})$ band of poly(vinyl alcohol) [14]. An analogous band at 620 cm^{-1} in bromal hydrate is less certain. The remaining bands are very probably due to skeletal vibrations. Two bands near 1100 cm^{-1} are likely due to mainly C—O stretching vibrations, and those between 900 and 700 cm^{-1} to the stretching vibrations of the C—CX₃ group. The skeletal bands of bromal hydrate are, as expected, somewhat lower than those of chloral hydrate. Some of the skeletal bands lie close together; this is not due to crystal splitting because the same bands occur in the solution spectra.

The spectra of crystalline monomethylalcoholates $[\text{CX}_3\text{CH}(\text{OH})\text{OCH}_3]$ have similar CH, OH and skeletal bands to the hydrates. There is considerably less splitting of the OH and CH bands. New bands, due to the methoxy groups, are easily distinguished (Table 2).

[14] S. KRIMM, C. Y. LIANG and G. B. B. M. SUTHERLAND, *J. Polymer Sci.* **22**, 227 (1956).