Hydrogen Bonding Features of Hexachloro-2-propanol. Part 1. A Near Infrared Study of Its Hetero-association with Oxygen-containing Bases

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Fig. 1. Illustrative spectra for the system HCP – DMSO. Solvent CCl_4, temperature 25 °C, path length 20 mm. Curve 1, 0.00418 M HCP, CCl_4 in the reference beam; curve 2, 0.00418 M HCP + 0.00401 M DMSO, 0.00401 M DMSO in the reference beam.

In a recent, rather extensive study of fluorinated alcohols, special attention was paid to spectral and association properties.[1,2] Now the investigation has been extended to the analogous chlorinated alcohols to discover what influence the substitution of chlorine for fluorine has on the hydrogen bonding ability. 1,1,1,3,3,3-Hexachloro-2-propanol (HCP) was chosen as the model compound since its fluoro-analogue, 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), has been extensively studied by us.

Earlier we have published a study on the hetero-association of HFP.[2] Here we report experimental data for the hetero-association of HCP with some proton acceptors.

Experimental. Chemicals. Hexachloro-2-propanol (Hynes Chemical Research Corp.) was purified by crystallization from hexane and dried in a desiccator with P_2O_5. Diphenyl sulfoxide (Aldrich Chemical Co.) was crystallized from hexane. The purification of the other chemicals has been reported previously.[2]

Measurements. The spectra were recorded on a Beckman DK-2A spectrophotometer equipped with a thermostated cell holder as described previously.[2] The path lengths of the cells were 20 mm. CCl_4 was used as solvent and the alcohol concentrations were sufficiently low to ensure that the alcohol was almost completely in the monomeric form. The concentrations were corrected for the thermal expansion of the solvent. At least two independent series of measurements were made for each alcohol – base pair.

Results and discussion. The free νOH absorption of HCP is a doublet (Fig. 1), the two peaks being somewhat more separated than in the case of HFP whose νOH absorption also comprises two peaks. The doublet nature of the νOH absorption is obviously due to the presence of two different conformers.[1] The experimental results obtained for various HCP – base systems are presented in Table 1, which includes also the corresponding values for HFP – base systems. The frequency shifts $\Delta\nu$OH are reported relative to the upper frequency of absorption of the free OH group occurring at about 3596 cm^{-1} in CCl_4 (the other peak of
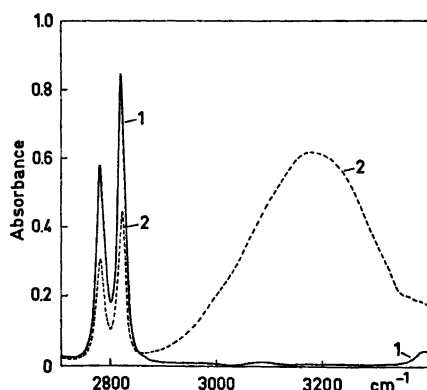
the doublet is at 3545 cm^{-1}). The equilibrium constants K_c (M^{-1}) were calculated as described previously from absorbance values observed before and after complex formation.[2]

When N,N-dimethylacetamide, tetramethylurea, diphenyl sulfoxide, or dimethyl sulfoxide was used as a base, the absorptions of the bonded νOH were uniform and the estimation of the frequency shifts ($\Delta\nu$) was easy. The absorption due to the bonded OH group of the HCP – acetone complex has a pronounced shoulder on the high-frequency side of the main band. This kind of band form is common when there is hydrogen bonding to a carbonyl oxygen. A reasonable explanation is the one given by Joris and Schleyer,[5] viz., that there are two bonding sites to which the proton can attach. The frequency shift for the HCP – acetone system is estimated from the main maximum.

When hexamethylphosphoric triamide (HMPA) was used as the proton acceptor, only a lower limit for $\Delta\nu$OH could be estimated because of the irregular form of the complex absorption. A similar irregularity in the hydrogen-bonded OH absorption is observed also in other HMPA complexes with alcohols or phenols of relatively great acidity.[4] The obvious reason for this is the relatively strong hydrogen bonds formed by HMPA; these will be discussed later in another connection.

The data in Table 1 reveal that the hydrogen bonds formed by HCP are relatively strong. However, the proton donating power of HFP is still somewhat more pronounced than that of HCP, as indicated by the greater values of K_c and $-\Delta H$ for the former compound. In Fig. 2 the values of $\Delta\nu$OH for the HCP – base complexes are plotted against the values of

Table 1. Values of spectrometric quantities for hydrogen bonding between hexachloro-2-propanol or hexafluoro-2-propanol (from Ref. 2) and various bases. Solvent CCl_4. Abbreviations: DMA = N,N-dimethylacetamide, TMU = tetramethylurea, DPSO = diphenyl sulfoxide, DMSO = dimethyl sulfoxide, HMPA = hexamethylphosphoric triamide.

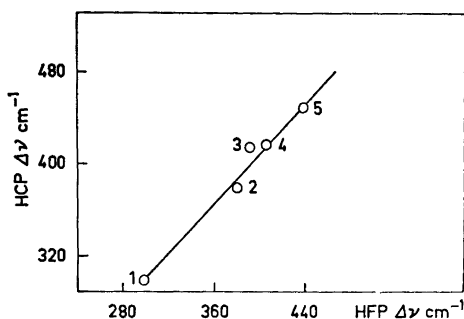| Base	t	HCP			HFP		
	$°C$	$\dfrac{K_c}{M^{-1}}$	$\dfrac{-\Delta H}{kJ\ mol^{-1}}$	$\dfrac{\Delta\nu OH}{cm^{-1}}$	$\dfrac{K_c}{M^{-1}}$	$\dfrac{-\Delta H}{kJ\ mol^{-1}}$	$\dfrac{\Delta\nu OH}{cm^{-1}}$
Acetone	0	23.7			118		
	25	11.1	21.0	300	49.0	24.9	297
	50	5.65			22.1		
DMA	0	509			5270		
	25	188	27.6	418	1520	32.1	405
	50	77.9			550		
TMU	0	688			4470		
	25	233	28.7	413	1300	33.7	390
	50	97.1			432		
DPSO[a]	0	183			1380		
	25	78.2	22.1	379	448	30.7	378
	50	40.7			172		
DMSO	0	826			3730		
	25	292	27.3	449	1430	29.2	437
	50	129			609		
HMPA[b]	15	6050			37 000		
	25	3960	33.3	>552	23 600	37.3	>519
	50	1360			7140		

[a] Ref. 3. [b] Ref. 4.

Fig. 2. The values of $\Delta\nu OH$ for the HCP − base systems plotted against the values of $\Delta\nu OH$ for the HFP − base systems. Base: 1 acetone, 2 diphenyl sulfoxide, 3 tetramethylurea, 4 N,N-dimethylacetamide, 5 dimethyl sulfoxide. The radii of the circles are of the order of experimental uncertainty.

Table 2. Values of $\Delta G°$ and $\Delta S°$ for the hydrogen bonding between HCP and bases. For abbreviations, see Table 1.

Base	$\dfrac{-\Delta G°}{kJ\ mol^{-1}}$	$\dfrac{-\Delta S°}{J\ mol^{-1}\ K^{-1}}$
Acetone	5.68	50.5
DMA	12.9	47.3
TMU	13.4	49.9
DPSO	10.9	35.3
DMSO	13.9	42.5
HMPA	20.1	40.3

$\Delta\nu$ for HFP − base complexes. The relationship is seen to be linear within experimental accuracy.

The values of $-\Delta H$, $-\Delta G°$, and $-\Delta S°$ (Table 2) for the HCP − diphenyl sulfoxide system are somewhat smaller than would be expected when compared for instance with the related values for HCP − acetone or HFP − diphenyl sulfoxide systems. This may be due,

at least in part, to steric hindrance of the relatively bulky trichloromethyl groups of HCP or of the phenyl groups of diphenyl sulfoxide.

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Table 1. Partial molal volumes, infinite dilution, 25 °C, ml mol^{-1}.

$-COOH$	25.9	
$-CH_3$	26.1	
$-CH_2-$	16.0	
$-CH_2COO-$	33.7	$(13 + 20.7)$

Table 2. Partial molal volumes at infinite dilution, 25 °C, ml mol^{-1}.

n	Exp.	Calc.	Diff.
A; $CH_3(CH_2)_nCOOH$			
0	51.9	52.0	-0.1
1	67.9	68.0	-0.1
2	84.6	84.0	0.6
3	100.5	100.0	0.5
4	116.0	116.0	0
B; $(CH_2)_n(COOH)_2$			
0	50.2	51.8	-1.6
1	67.2	67.8	-0.6
2	82.9	83.8	-0.9
3	99.1	99.8	-0.7
4	115.7	115.8	-0.1
5	131.9	131.8	0.1
C; $CH_3(CH_2)_nCOO-$			
0	45.8		
1	60.3	59.8	0.5
2	75.8	75.8	0
3	91.7	91.8	-0.1
4	107.2	107.8	-0.6
D; $COOH(CH_2)_nCOO^-$			
0	45.7	(46.6)	(1.2)
2	75.5	75.6	-0.1
3	91.4	91.6	-0.2
4	107.6	107.6	0
5	123.2	123.6	-0.4
E; $(CH_2)_n(COO^-)_2$			
0	41.3	(41.4)	(-0.1)
2	67.3	67.4	-0.1
3	83.2	83.4	-0.2
4	99.4	99.4	0
5	115.0	115.4	-0.4

Additivity Relations of Partial Molal Volumes in Carboxylic Acid Series

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It has been shown by a number of workers that the partial molal volumes of electrolytes at infinite dilution are equal to the sum of the ionic components (see Ref. 1). Clearly, as Millero[1] points out, the utility of partial molal volumes to study ion − water interactions lies in the additivity principle.

Only a CH_2-group, with its volume requirements, separates two successive members of a homologous series of carboxylic acids. As early as 1899 Traube[2] found that the partial molal volume of a CH_2-group in aqueous solution was on the average 16.0 ml mol^{-1}. This has been verified by the data of Sakurai.[3] In this paper data at 25 °C obtained by King,[4] Sakurai,[3] and Høiland[5] have been used to investigate the additivity of the partial molal volumes of the groups comprising the carboxylic acid or the acid anion.

Results. Two requirements must be fulfilled in order to calculate the partial molal volumes of the different groups involved. First, the well documented starting point that the partial molal volume of a CH_2-group is 16.0 ml mol^{-1}. Second, the partial molal volume of the sodium ion is required in order to obtain the partial molal volume of the carboxylate ion. The best value of $\bar{V}^0(Na^+)$ is probably found by taking Zana and Yeager's[6] value for $\bar{V}^0(H^+) = -5.4 \pm 0.2$ ml mol^{-1}, and add the experimentally determined difference $\bar{V}^0(H^+) - \bar{V}^0(Na^+) = -1.2$ ml mol^{-1}. Thus $\bar{V}^0(Na^+) = -6.6$ ml mol^{-1}. This was used, and the experimental data are given in Table 2. The value of $\bar{V}^0(Na^+)$ does not affect the additivity principle, only

the partial molal volume of the COO$^-$ group.

With $\bar{V}^0(CH_2) = 16.0$ ml mol^{-1} average values of the partial molal volume of the COOH group were calculated from series A and B, Table 2, CH$_3$ group values from A and C. Results are summarized in Table 1. A charged carboxyl group influences the hydration sphere of the nearest neighbouring CH$_2$ group substantially.[7] Separation of the partial molal volumes of the COO$^-$ group and the nearest CH$_2$ group will therefore be ambiguous. The partial molal volumes from series C, D, and E (Table 2) are given as $\bar{V}^0(CH_2COO^-)$ in Table