

Fluoroalcohols

Part 15.¹ A Near-Infrared Study of the Self-Association of Trifluoro and Hexafluoro Substituted Tertiary Butyl Alcohols. A Model for the Structures of Alcohol Associates

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The self-association of 2-trifluoromethyl-2-propanol and 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol in carbon tetrachloride solutions has been studied at temperatures from 0 to 60°C. The tendency of the former alcohol to undergo self-association was found to be somewhat more marked than that of the latter, which does not seem to exist as higher associates than dimers even in the neat liquid. The forms of the OH stretching vibration bands are discussed. The densities of 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol-carbon tetrachloride mixtures at 25 and 40° are reported.

The structures of alcohol dimers in general as well as the frequency shift values $\Delta\nu(\text{dim})$ of the dimers relative to the monomer absorption band are discussed. The experimentally observed solvent dependences of the values of $\Delta\nu(\text{dim})$ for various alcohols and values reported in the literature for the dielectric properties of solutions of alcohols in inert solvents suggest that the self-association of alcohols in carbon tetrachloride proceeds with increasing alcohol content through the steps: monomer-cyclic dimer-linear dimer-(linear trimers and/or higher linear associates)-cyclic trimers or tetramers. This association sequence is discussed in the light of other available data for the alcohols.

In earlier parts of this series, we have described properties of fluorinated alcohols, especially those of 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP).¹⁻³ The self-association of TFE and HFP was discussed in Part 2² and the conformations of these and some other fluoroalcohols in Part 3.³ Near-infrared spectroscopy was employed in the investigations. Quite recently, Fletcher and Heller⁴ questioned the existence of significant amounts of dimers in dilute solutions of alcohols in inert solvents.

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This led us to continue our work on the self-association of alcohols. This paper deals with the properties of 2-trifluoromethyl-2-propanol (trifluoro-*t*-butyl alcohol, TFTB) and 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol (hexafluoro-*t*-butyl alcohol, HFTB). For comparison, some measurements were made also on 2-methyl-2-propanol (*t*-butyl alcohol, TB) and methanol.

EXPERIMENTAL

Chemicals. TFTB (Pierce Chemical Co., Rockford, Ill.) was distilled in a Todd Fractionation Assembly at a reflux ratio of 1 : 10. The product boiled at 81–82°/767 mmHg (lit. 81.6°,^{5a} 80–81°^{5b} at atm. pressure). HFTB (Hynes Chemical Research Corp., Durham, N.C.) was purified by distillation through a 20 cm Vigreux column; the product boiled at 62–63°/764 mmHg (lit.⁶ 62°). Methanol and 2-methyl-2-propanol were purified by conventional methods. Solutions of the alcohols in carbon tetrachloride were prepared as previously.²

Spectrophotometric measurements. These were carried out with a Beckman DK-2A Ratio Recording Spectrophotometer; the instrumental conditions were similar to those used previously.^{2,3} In most cases, the recordings were first made at 25°, then at the other temperatures, and finally a second time at 25° to ascertain whether evaporation (which could have led to considerable errors in absorbance values,⁷ see p. 916) had occurred. The concentrations were corrected for the thermal expansion of the solvent. Densities were measured with a pycnometer of 3 ml capacity, the weighings being corrected to vacuum.

The non-SI units used were: 1 cal = 4.184 J; 1 M = 1 mol dm⁻³; 1 mmHg = 133.322 N m⁻².

CALCULATIONS AND RESULTS

The monomer-dimer equilibrium constants K_c (M⁻¹) were calculated as previously² by the method of Liddel and Becker⁸ from initial slopes of plots of the apparent molar absorption coefficient ϵ_m at the maximum of the monomer ν_{OH} absorbance against the molar concentration of the alcohol assuming the dimers to be cyclic. Values of the thermodynamic parameters were obtained in the usual way from plots of $\log K_c$ against $1/T$. The results for the alcohols studied are given in Table 1. The densities of the HFTB–CCl₄ mixtures are given in Table 2.

Table 1. Monomer-dimer equilibrium constants K_c (M⁻¹) and molar absorptivity coefficients at infinite dilution ϵ_m° (M⁻¹ cm⁻¹) of fluorinated *t*-butyl alcohols in carbon tetrachloride.

Alcohol	Region	$t^\circ\text{C}$	K_c	ϵ_m°
CF ₃ (CH ₃) ₂ COH	Fundamental	0	1.07	132
		15	0.65	125
		25	0.51	121
		40	0.39	115
		60	0.26	108
(CF ₃) ₂ CH ₃ COH	First overtone	0	0.33	1.32
		15	0.25	1.32
		25	0.22	1.34
		40	0.18 ₁	1.34
		50	0.15 ₆	1.35

Table 2. The densities (g cm^{-3}) of hexafluoro-*t*-butyl alcohol-carbon tetrachloride mixtures.

25°				40°			
(CF ₃) ₂ CH ₃ COH			d_4^{25}	(CF ₃) ₂ CH ₃ COH			d_4^{40}
Wt. %	Mol fraction	Molar conc.		Wt. %	Mol fraction	Molar conc.	
100	1.0000	8.151	1.4837	100	1.0000	7.955	1.4481
77.6	0.7854	6.327	1.4835	77.6	0.7854	6.176	1.4481
65.4	0.6148	5.352	1.4901	65.4	0.6148	5.227	1.4555
51.3	0.4709	4.232	1.5017	51.3	0.4709	4.135	1.4673
37.3	0.3350	3.114	1.5176	37.3	0.3350	3.046	1.4847
31.5	0.2804	2.644	1.5256	31.5	0.2804	2.588	1.4932
24.9	0.2006	2.102	1.5350	24.9	0.2006	2.059	1.5037
21.3	0.1859	1.801	1.5417	21.3	0.1859	1.764	1.5100
16.9	0.147	1.438	1.5477	16.9	0.147	1.409	1.5167
14.0	0.121	1.198	1.5538	14.0	0.121	1.175	1.5240
10.0	0.0863	0.861	1.5610	10.0	0.0863	0.854	1.5314
0	0.0000	0		0	0.0000	0	

DISCUSSION

The forms of the OH stretching vibration bands. It is well known that the OH stretching vibration bands in the spectra of many saturated alcohols are symmetric. Recently, Joris *et al.*⁹ thoroughly discussed the forms of these bands and gave numerous references to previous studies. They concluded that the asymmetry is best explained to be due to conformational heterogeneity. According to this view, each C-O rotational isomer (rotamer) gives rise to a symmetric OH absorption. Therefore, molecules with only one minimum energy rotamer have symmetric absorption bands. The view of Joris *et al.*⁹ is, in principle, similar to that of Ōki and Iwamura.¹⁰ The former authors reinvestigated the spectra of methanol, ethanol, 2-propanol, and *t*-butyl alcohol and confirmed the previous results, *i.e.*, that the OH absorption bands of methanol and *t*-butyl alcohol are symmetric and those of ethanol and 2-propanol asymmetric.

In Part 3³ we discussed the fundamental ν_{OH} absorption bands and conformations of some fluoroalcohols. We deduced that the hydroxyl group may be free, hydrogen bonded to one fluorine atom, or simultaneously hydrogen bonded to two fluorine atoms (bifurcated bonding; we use this term to describe a hydrogen bond in which the hydrogen atom is more or less equidistant from two acceptor atoms¹¹). There has been some scepticism as to the existence of bifurcated bonds.¹² However, there is ample evidence for the existence of such hydrogen bonding in solids,¹¹ and we assume that this kind of bonding may exist also in solutions (see, *e.g.*, Ref. 13).

The papers of Wyn-Jones and Orville-Thomas¹⁴ and of Buckley *et al.*¹⁵ are interesting. They studied the rotational isomerism of, for example, 2-fluoroethanol. In both papers it is stated that the alcohol exists almost solely

in the *gauche* form. This statement is in disagreement with the opinion of Krueger and Mettee.¹⁶

Recently, Gounelle and Jullien,¹⁷ when studying the intramolecular hydrogen bonding $\text{OH}\cdots\text{Hal}$ of several halogenated alcohols, deduced that these alcohols occur as two conformers. One of these contains a free hydroxyl group and absorbs at higher frequencies; the other contains a "bonded" hydroxyl group.

It may also be mentioned that Khairtadinova and Pereygin¹⁸ studied the forms of the fundamental absorption bands of OH stretching vibrations of several chloro-substituted alcohols. Qualitatively, the shapes of the absorption bands of these alcohols are similar to those of the fluoro analogues. Their explanation is similar to ours for the corresponding fluoroalcohols;³ for example, they consider that the hydroxyl hydrogen may lie between two CCl_3 groups in one rotational isomer of hexachloro-2-propanol. (See Ref. 19 for a discussion of $\text{OH}\cdots\text{halogen}$ interactions.)

The shapes and locations of the fundamental OH stretching absorption bands of TB, TFTB, and HFTB in their dilute solutions in carbon tetrachloride at 25° are shown in Fig. 1. The band of TB is seen to be symmetric. Its maximum is at 3613 cm^{-1} , assuming the band of TFE to be located at 3619 cm^{-1} as was done previously² (cf. also Refs. 9 and 20). The band of TFTB resembles that of TB in form and its maximum is at 3603 cm^{-1} . The band of HFTB is, however, composed of two peaks, a smaller one at 3608 cm^{-1} and a larger one at 3581 cm^{-1} . Two ν_{OH} absorption peaks were observed³ also in the spectrum of HFP in CCl_4 ; these were at 3615 cm^{-1} and 3578 cm^{-1} . It may be mentioned that the OH absorption band of perfluoro-*t*-butyl alcohol is located at 3610 cm^{-1} ; ^{21a} the band (vapour) is symmetric.^{21b}

In accordance with the explanation given in Part 3,³ we assume that TFTB exists mainly in the form where the OH group is bonded to one fluorine

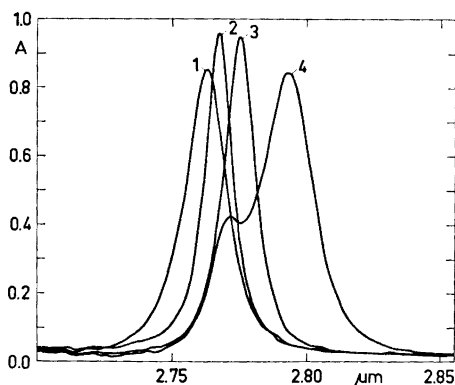


Fig. 1. Shapes of monomeric OH stretching bands of alcohols (fundamental region) in CCl_4 at 25°. Path length 10 mm. 1, 0.00718 M 2,2,2-trifluoroethanol; 2, 0.0135 M 2-methyl-2-propanol; 3, 0.00774 M 2-trifluoromethyl-2-propanol; 4, 0.00729 M 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol.

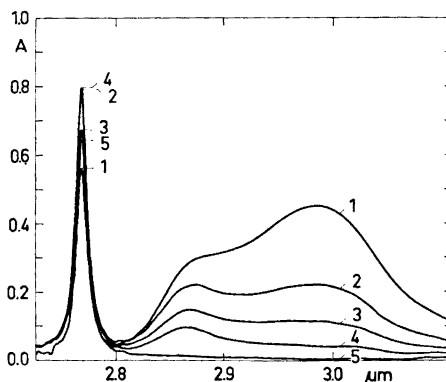


Fig. 2. Illustrative spectra of 2-methyl-2-propanol (fundamental region) in CCl_4 at 25°. Molar concentrations (cell thicknesses in mm in parentheses): 1, 0.293 (0.5); 2, 0.157 (1); 3, 0.126 (1); 4, 0.069 (2); 5, 0.0052 (20).

atom, whereas this kind of bonding is less marked in the case of HFTB, the stronger absorption of which at the lower wavenumber may be due to simultaneous bonding of the OH group to two fluorine atoms.

Self-association. It is known² that fluoroalcohols are less associated than the corresponding unsubstituted alcohols. This is evident also on inspection of data for fluorinated *t*-butyl alcohols (Figs. 2–4). At TB concentrations of 0.1–0.2 M (Fig. 2), there is a moderately strong dimer band at about 3500 cm^{-1} and a polymer band. When the TB concentration exceeds 0.2 M, the polymer band becomes greater than the dimer band and the latter begins to merge into the polymer band. In the case of TFTB (Fig. 3), however, we note almost solely a dimer absorption band at a concentration of 0.06 M. As seen from Fig. 4, the tendency of HFTB to undergo self-association is still

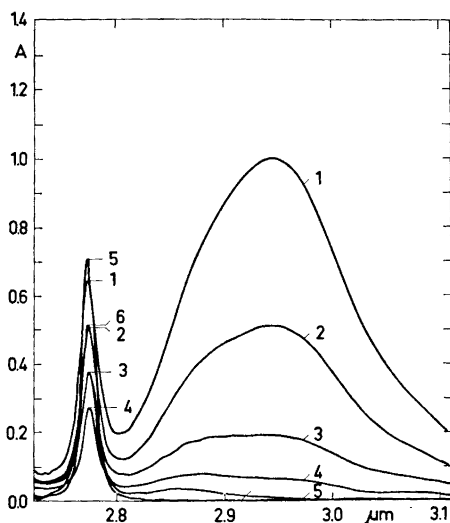


Fig. 3. Illustrative spectra of 2-trifluoromethyl-2-propanol (fundamental region) in CCl_4 at 25°. Molar concentrations (cell thicknesses in mm in parentheses): 1, 1.48 (0.1); 2, 0.890 (0.1); 3, 0.472 (0.1); 4, 0.297 (0.1); 5, 0.0631 (1); 6, 0.00426 (10).

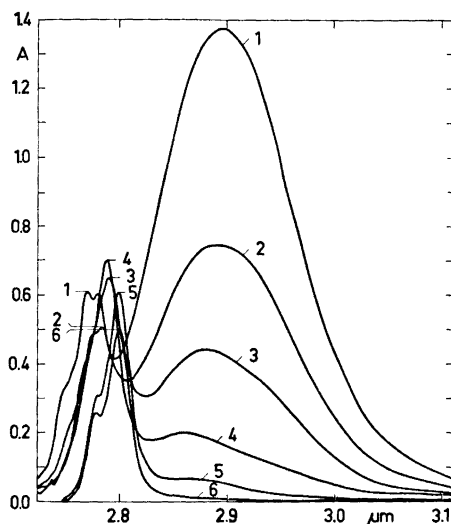


Fig. 4. Illustrative spectra of 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol (fundamental region) in CCl_4 at 25°. Molar concentrations (cell thicknesses in mm in parentheses): 1, 8.15 (neat alcohol; 0.02); 2, 5.46 (0.02); 3, 2.17 (0.05); 4, 0.782 (0.1); 5, 0.335 (0.2); 6, 0.002 (20).

weaker; even at a concentration of 0.8 M the dimer content is not very high and there is no sign of higher polymers even in neat HFTB.

As mentioned, Fletcher and Heller⁴ have questioned the interpretation of the "dimer" band. Their arguments, however, seem to be based on an incorrect interpretation of the band at 1.53 μm (about 6530 cm^{-1}), which they considered to be an overtone of the 2.86 μm (about 3500 cm^{-1}) band.^{22,23} There seems to be no doubt that the band at 2.86 μm indicates the presence of dimers and, as stated above, the dimer is obviously the largest associate present in pure HFTB. Even in the pure alcohol the concentration of dimers is not very

high (since the integrated intensities of the dimer and polymer bands are much greater than those of the free OH bands²⁴). The reverse is true for ordinary alcohols; for example, Storek and Kriegsmann²⁵ deduced from NMR measurements that the fraction of dimers is low in solutions of TB in carbon tetrachloride at TB concentrations greater than 0.08 M (*cf.* Fig. 2).

The question concerning the preponderance of open or cyclic dimers of alcohols (and phenols) has not yet been settled (for a recent review, see Ref. 19). However, it is probable that this preponderance may vary with the structure of the alcohol (*cf.*, *e.g.*, Ref. 26). Bellamy and Pace²⁷ have investigated this problem in an elegant way by studying the association between methanol and phenol. They deduced that the methanol dimers are linear. Also this work has been criticized, and it has been stated²⁸ that the results Bellamy and Pace obtained concerning heteroassociation do not necessarily hold in the case of self-association. On the other hand, Van Ness *et al.*²⁸ (*cf.* Refs. 30 and 31) deduced that no mathematical model which neglects the cyclic dimer is likely to prove satisfactory.

We now turn to the question of the structure of the alcohol dimers. When studying the self-association of di-*t*-butyl carbinol in carbon tetrachloride, Patterson and Hammaker²⁸ collected, in addition to their own data, also literature values for some simple alcohols. The value of $-\Delta H$ for the dimer formation diminishes from slightly over 9 to below 5 kcal mol⁻¹ in the order methanol, ethanol, 2-propanol, and *t*-butyl alcohol and the value of ΔS^* increases from -28 cal K⁻¹ mol⁻¹ (methanol) to -11 cal K⁻¹ mol⁻¹ (*t*-butyl alcohol). Patterson and Hammaker concluded that the dimer of *t*-butyl alcohol (as well as that of di-*t*-butyl carbinol) is probably linear, whereas considerable fractions of the dimers of methanol and ethanol are cyclic. Table 3 contains data for some fluoroalcohols. If we accept the view of Patter-

Table 3. Values of K_c , ΔH° , ΔG° , and ΔS° for the dimerization of some fluoroalcohols in carbon tetrachloride solutions at 25°.

Alcohol	K_c l mol ⁻¹	ΔH° kcal mol ⁻¹	ΔG° kcal mol ⁻¹	ΔS° cal K ⁻¹ mol ⁻¹	Ref.
CF ₃ CH ₂ OH	0.65	-5.33	0.24	-18.7	2
(CF ₃) ₂ CHOH	0.13	-5.53	1.23	-22.7	2
CF ₃ (CH ₂) ₂ COH	0.49	-3.68	0.40	-13.7	This work
(CF ₃) ₂ CH ₂ COH	0.22	-2.74	0.90	-12.2	This work

son and Hammaker, the data for fluoroalcohols can be explained by assuming that the dimers of TFTB and HFTB are linear, whereas the data for TFE and HFP² are best explained by assuming the dimers to be cyclic. However, this view is not in accordance with the discussion below.

For most alcohols (and phenols), the polymer frequency shifts $\Delta\nu(\text{pol})$ ($=\nu(\text{polymer})-\nu(\text{monomer})$) are more than twice as great as the dimer frequency shifts $\Delta\nu(\text{dim})$ (which are usually about 125 cm⁻¹ (Ref. 32)). In another connection³³ we have noted that $\Delta\nu(\text{dim})$ for several alcohols varies

Table 4. Values of $\Delta\nu(\text{dim})$ in cm^{-1} for the self-association of methanol in dilute carbon tetrachloride solutions (fundamental OH stretching). Values in parentheses are only approximate.

0.5°C		25°C		50°C	
c_{MeOH}	$\Delta\nu$	c_{MeOH}	$\Delta\nu$	c_{MeOH}	$\Delta\nu$
0.00764	(107)	0.00656	(92)	—	—
0.0153	113	0.0131	(98)	0.0144	(94)
0.0306	124	0.0263	103	0.0288	100
0.0764	145	0.0736	121	0.0719	108
0.153	(150)	0.147	144	0.144	120
		0.298	(147)	0.289	135
		0.746	—	0.723	(155)

considerably with concentration. We carried out measurements also with methanol (Table 4) and noted a very large change of $\Delta\nu(\text{dim})$ in the dimerization of this alcohol, the value of $\Delta\nu(\text{dim})$ being about 90–110 cm^{-1} in the most dilute solutions where the dimer absorption begins to be perceptible and about 145 cm^{-1} at a methanol concentration of 0.15 M (estimation of $\Delta\nu(\text{dim})$ in more concentrated solutions is not possible because of strong polymer absorption).

$\Delta\nu(\text{dim})$ increases from about 88 cm^{-1} in dilute solutions of HFTB in CCl_4 to about 145 cm^{-1} in the neat alcohol at 25°. These shifts were measured from the absorption maximum at 3608 cm^{-1} ; if the shoulder at higher wavenumber is used (Fig. 1), the shifts are 114 cm^{-1} and 158 cm^{-1} , respectively. In the case of TFTB, $\Delta\nu(\text{dim})$ increases from 111 cm^{-1} (0.014 M alcohol) to 130 cm^{-1} (0.16 M alcohol), the value of $\Delta\nu(\text{pol})$ being about 282 cm^{-1} in the latter case. In the case of TB, $\Delta\nu(\text{dim})$ increases from 120 cm^{-1} (0.01 M) to 142 cm^{-1} (0.26 M); in more concentrated solutions, the dimer absorption merges with the polymer absorption. It should be mentioned that the difference between the wavenumber values of the two peaks of the monomeric OH doublet band of HFTB seems to be concentration dependent. It is difficult to decide whether this is due to the influence of the solvent or to band overlapping; it is also possible that the relative abundances of the two conformers of the alcohol monomers (p. 907) vary with the alcohol content of the solution.

There is the possibility that the increasing polymer absorption shifts the dimer absorption maximum. However, there are cases such as 2,2,4-trimethyl-3-pentanol,³³ where the dimer shift is very marked and there is practically no polymer absorption. The concentration dependence may in part be explained as being induced by the solvent (*cf.* Ref. 34), but this explanation seems to be inappropriate as, for example, in the case of methanol in CCl_4 , the solvent changes very little in the concentration range where the dimer shift is observed (Table 4) (*cf.* Ref. 33). As we noted in another connection,³³ the change is best explained by assuming that the alcohol dimers are mainly cyclic in the most dilute solutions, and the fraction of linear dimers present in solution increases with increasing alcohol content.

It can also be concluded that the discrepancies in reported³² values of $\Delta\nu(\text{dim})$ are not necessarily due to experimental uncertainty, but are results of the different concentrations employed by different investigators³³ (*cf.* Ref. 34).

Singh and Rao³⁵ have studied the self-association of TFE and 2,2,3,3-tetrafluoro-1-propanol (TFP) in benzene, as these fluoroalcohols are only sparingly soluble in carbon tetrachloride. These results are thus not directly comparable with those obtained in the present study. The values they reported for $\Delta\nu(\text{dim})$ (230 cm^{-1} for TFE and 190 cm^{-1} for TFP) are exceptionally high. They are of the same order of magnitude as found² for the polymer shifts in carbon tetrachloride. For example, the polymer shift for TFE is 244 cm^{-1} and the dimer shift only about 100 cm^{-1} .²

It is interesting to note that Singh and Rao obtained for $-\Delta H$ the values 3.8 kcal mol^{-1} (TFE) and 1.2 kcal mol^{-1} (TFP). The former value is of the expected magnitude, as the values in benzene are usually slightly less negative than those in CCl_4 (*cf.* Table 3), but the latter is exceptionally low.

The most convincing arguments in favour of the cyclic structure of alcohol dimers in very dilute solutions in inert solvents emerge from dielectric measurements (*e.g.*, Refs. 36–39; *cf.* Refs. 30 and 40–43). The correlation parameter g of the Kirkwood-Fröhlich equation^{44,45} has been measured for a great number of alcohol-inert solvent systems (and also for neat alcohols). The fact that g is less than unity for dilute solutions indicates that in most alcohol complexes in dilute solutions the dipoles are oriented antiparallel. (The value $g=1$ at infinite dilution means that there is no correlation between the dipole moments of the alcohol molecules, *i.e.*, the solution contains monomers so far apart that the individual dipoles are randomly oriented.) The small g values in dilute alcohol solutions can hardly be explained without assuming that at least a considerable fraction of the alcohol dimers consists of cyclic dimers. It is interesting to note that lowering the temperature causes g to decrease in the low-concentration region and to increase in the high-concentration region (for pure alcohols, g is usually large, approximately 2.5–3.1). Apparently both open-chain and cyclic structures become more stable with decreasing temperature.

We thus deduce that the values of $\Delta\nu(\text{dim})$ in the range 90–110 cm^{-1} are due to the cyclic alcohol dimer in the most dilute solutions, and those approaching the value 160 cm^{-1} found in more concentrated solutions are due to the linear dimer. It is possible that in cases where the lower limit is about 120 cm^{-1} linear dimers are present already in very dilute solutions.

We note that the upper limit of $\Delta\nu(\text{dim})$, about 150–160 cm^{-1} , is close to the values 157 cm^{-1} ⁴⁶ and 159 cm^{-1} ⁴⁷ found for the intramolecular frequency shift of 1,4-butanediol in CCl_4 (in the vapour phase, the frequency shift is only 110 cm^{-1}). The intramolecular bonding in 1,4-butanediol is somewhat similar to that in linear alcohol dimers. It is interesting to note that double chelation has been proposed for some diols.⁴⁸

The results for dilute solutions of alcohols in inert solvents can be compared with those obtained by the matrix isolation technique, which enables the identification of bands due to monomers, dimers, *etc.*, as each of these gives rise to a relatively narrow band at the low temperatures employed. In their classical work, Van Thiel *et al.*⁴⁹ found several peaks in the methanol spectrum

(nitrogen matrix at 20 K) which they attributed to different polymer species (monomer, dimer, trimer, *etc.*).

Recently, Barnes and Hallam⁵⁰ discussed the IR spectrum of methanol in an argon matrix. In addition to the monomer band, Barnes and Hallam found absorption bands at locations 139, 172, 221, and 298 cm^{-1} from the monomer absorption band. They explained these bands as being due to open dimer, open trimer, open tetramer and cyclic tetramer absorptions. On the basis of their matrix isolation studies, Barnes and Hallam proposed a model for self-association of alcohols very similar to that described in the present paper. However, we are of the opinion that it is necessary to propose also the presence of appreciable amounts of cyclic alcohol dimers in dilute carbon tetrachloride solutions at about room temperature.

Barnes and Hallam⁵⁰ also noted an oligomer band on the *high* frequency side of the monomer band which might be due to the free OH (OD) absorption of an open-chain oligomer structure.²⁷

Comparisons of values of $\Delta\nu(\text{dim})$ for dilute CCl_4 solutions with the values for the gas phase seem to be few in number. Reece and Werner⁵¹ reported values of $\Delta\nu$ for the association of alcohols with various types of proton acceptors both in the vapour phase and in dilute CCl_4 solutions. The frequency shifts of 1 : 1 complexes were on the average 15 % higher in CCl_4 than in the vapour (in a few cases the difference was as high as 40–50 %; the values of $\Delta\nu$ in the vapour phase varied between 58 and 370 cm^{-1}).

Reece and Werner have reported the values 88 cm^{-1} (vapour) and 111 cm^{-1} (CCl_4) for $\Delta\nu(\text{dim})$ for the self-association of methanol at 25°. Values reported by Allerhand and Schleyer⁵² are 90 cm^{-1} (vapour) and 121 cm^{-1} (CCl_4). Thus the value in the vapour phase does not differ greatly from the lowest value of $\Delta\nu(\text{dim})$ for methanol dimers in the most dilute CCl_4 solutions (Table 4). It is, however, questionable if this can be taken as evidence that the methanol dimer is similar in structure in the vapour phase and in carbon tetrachloride.

It may be somewhat dangerous to compare self-association and hetero-association, especially as the ΔH values reported for the dimerization of alcohols may be affected by cyclic dimer-open dimer equilibria (see p. 909). We feel, however, that additional evidence concerning the existence of cyclic dimers can be obtained from plots of ΔH versus $\Delta\nu$. In Part 7⁵³ of this series, we reported values of ΔH and $\Delta\nu$ for various heteroassociates of TFE and HFP and found that the relationship between these quantities was approximately linear. From the plots of ΔH versus $\Delta\nu$ we can estimate that a value of ΔH of about -3 kcal mol^{-1} corresponds to a value of $\Delta\nu$ of about 90–100 cm^{-1} (remembering, however, that the estimation is more difficult at low than at high values of $\Delta\nu$, as the plot of ΔH against $\Delta\nu$ does not seem to pass through the origin).

The values of $-\Delta H$ for the dimerization of TFE and HFP are 5.3 and 5.1 kcal mol^{-1} , respectively. These correspond to values of $-\Delta H$ of about 2.5–2.7 kcal per bond , if we assume a cyclic form for the dimers. A value of this magnitude would be obtainable also from the $\Delta H - \Delta\nu$ plot; on the other hand, the values 5.1–5.3 $\text{kcal per hydrogen bond}$ (linear dimer) deviate from the plot. We estimated above that the frequency shift of the linear dimer is about 160 cm^{-1} ; according to the mentioned plot this would correspond to a

value of $-\Delta H$ slightly above 4.0 kcal mol⁻¹ (*i.e.*, 4.0 kcal per hydrogen bond).

The same discussion is applicable also to methanol. The spectroscopic values of $-\Delta H$ for the dimerization of methanol (and other simple alkanols) vary usually between 6 and 9 kcal mol⁻¹ (see, *e.g.*, the references given by Murthy and Rao⁵⁴). If there were only one hydrogen bond in the dimer, the values of about 90–110 cm⁻¹ for $\Delta\nu(\text{dim})$ and values of about 6 kcal mol⁻¹ for $-\Delta H$ should deviate more or less from the plot of $\Delta\nu$ versus ΔH for heterodimers (see Fig. 2 in Ref. 54). We do not see any reason why the point for an alcohol dimer should greatly deviate from a Badger-Bauer plot and thus conclude that the ΔH values refer to cyclic dimers in accordance with our general model (alternatively, the reported experimental values are influenced by the equilibrium between cyclic and linear dimers). It may be mentioned that also values of $-\Delta H$ varying from 3.5 to 4.0 kcal mol⁻¹ have been reported for the dimerization of methanol.⁵⁵ However, some of these values refer to the vapour state.

Some models of associates are presented in Fig. 5.

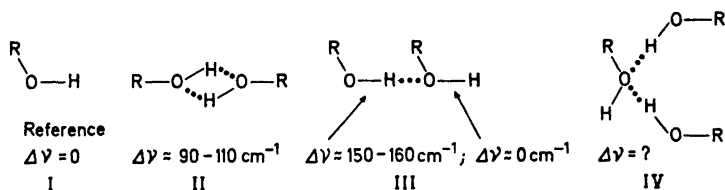


Fig. 5. Models proposed for alcohol dimers and the assumed frequency shifts. Concerning the proposed values of $\Delta\nu$ of higher associates and structure IV, see text.

The frequency shifts, *ca.* 240 cm⁻¹, found for higher polymers of TFE and HFP (see Part 2² in this series) would correspond, according to the above reasoning, to a value of $-\Delta H$ that slightly exceeds 5 kcal mol⁻¹. We consider this too high a value for a linear hydrogen bond. The value of $\Delta\nu$ reported for methanol polymers (about 280 cm⁻¹) seems even more too large a value for a hydrogen bond when compared with values for heterodimers of methanol.⁵⁴ On the other hand, we accept the view of Bellamy and Pace that in the associates of alcohols (and phenols) the hydrogen of the OH group acting as a proton acceptor is more acid and the oxygen of the donor OH group is more basic than in the monomers. These effects superimpose in cyclic structures and we can consider the hydrogen bonds of cyclic trimers or tetramers as being exceptionally strong. This is reflected in the large frequency shifts.

We believe that, in addition to the aggregates dealt with above, also trimers in which two ROH molecules are simultaneously bonded to one oxygen atom in a third molecule (structure IV in Fig. 5) may be of some importance. It is difficult to estimate the value of the frequency shift for such a trimer; it is, however, very probable that an addition of a third alcohol molecule does not change the value of the frequency shift appreciably from that found for linear dimers.

Our scheme for the self-association of alcohols resembles that of Bellamy,^{19,27,56} but the essential difference is that according to our opinion formation of cyclic dimers first occurs in the most dilute solutions and this is followed by formation of linear dimers. Our conclusions do not invalidate the results Bellamy and Pace²⁷ obtained by the cancellation technique, as these seem to have been based on measurements at methanol concentrations so high that a considerable fraction of the methanol dimers obviously were of the linear type.

The fact that the Kirkwood-Fröhlich correlation factor g has a relatively high value in pure alcohols, in many cases of the order of 2.5–3.2 (*e.g.* Ref. 38), could be taken as evidence pointing to a long chain structure of the associates (*cf.* Ref. 57). This is not necessarily true if we accept that also a cyclic structure containing at least three alcohol units can possess a considerable dipole moment.^{43,58} We thus conclude that merely on the basis of the g values, it is not necessary to abandon the assumption that larger alcohol associates have cyclic structures.

Also the influence of pressure on alcohol association has been studied,^{59–61} but the explanations given are somewhat contradictory. However, it is interesting to note the convincing experimental evidence of Jakobsen *et al.*⁶¹ which indicates the existence of a special absorption band due to the terminal OH group in spectra of neat alcohols. One of the alcohols investigated by them was 2,2,4-trimethylpentanol; in this case it is probable that the dimer is the largest associate. We have previously³³ proposed a linear structure for the dimer of this alcohol in solutions of high alcohol content. The results of Jakobsen *et al.* are in agreement with our own results for this alcohol.

Having accepted as our working hypothesis the association sequence monomer – cyclic dimer – (open trimer and/or higher linear associates) – cyclic trimer and/or tetramer with increasing alcohol concentration in carbon tetrachloride solutions, it is interesting to make some comparisons with some other studies. In their thorough paper, Van Ness *et al.*²⁹ compared infrared spectral data with heats of mixing of ethanol – heptane (and ethanol – toluene) mixtures. As mentioned above, they stressed the importance of cyclic dimers when devising models of association for alcohols. We agree with this, *i.e.*, if there is only one kind of alcohol dimer, this obviously is of the cyclic type (in dilute inert solvents), but, as discussed above, there is ample evidence for the existence of the linear dimer alongside the cyclic dimer.

Van Ness *et al.*²⁹ expressed the opinion that associates higher than the dimers are linear and that these give rise to the “polymer” band. We consider the reasoning of Van Ness *et al.* inadequate to explain shifts of the order of 280–300 cm^{-1} in the case of polymers of ordinary alcohols unless we assume special, cyclic structures for the polymers.

The article of Van Ness and coworkers is one of the few papers where a “water-like” structure has been considered, *i.e.*, a network structure which consists of units bound as in model IV in Fig. 5. These authors have found in their spectra a minor peak corresponding to a frequency shift of about 510 cm^{-1} . We consider such a large shift improbable for small associate units (*cf.* p. 911), but if there exist larger network structures (*e.g.*, at low temperatures),⁶² these could be held together by bonds of this kind and a large frequency

shift might be possible. It would then indicate bonds of very markedly increased strength as compared with other types of hydrogen bonds found in alcohols.

Despite the above alternatives we must note that the model of Van Ness *et al.*²⁹ seems to conform to thermodynamic conclusions.^{63,64}

Tucker *et al.*⁶⁵ studied the association of methanol in the vapour phase and in hexadecane by a vapour pressure method and concluded that the results are best explained by assuming the presence of only two associated species, trimers and octamers, of which the trimers are linear and octamers cyclic. They applied their model with success in an interpretation of IR and NMR data of other workers. They connect the absorption band shifted 130 cm^{-1} from the monomer absorption band with the terminal hydroxyl of a linear trimer, which functions only as a proton donor. Our model differs from their model in that the shift of 130 cm^{-1} arises simultaneously from the absorption of cyclic dimers and of the terminal hydroxyl groups of open dimers acting as proton donors. The main difference between our explanation of the shift of 280 cm^{-1} and that of Tucker *et al.* is that we propose that the associates are cyclic trimers or tetramers, whereas Tucker *et al.* favour cyclic octamers. We do not exclude the possibility of cyclic octamers, but we feel that smaller rings might be more stable (having in mind also the relatively short average lifetime of hydrogen bonds). The number of alcohol molecules in the associates may also vary from alcohol to alcohol.

It may be mentioned that Pauling⁶⁶ suggested that neat alcohols may consist largely of cyclic polymers. This supposition would account for the relatively small heats of fusion of alcohols, inasmuch as the transition from chains in the solid to cyclic aggregates in the liquid would not involve rupture of hydrogen bonds.

It must be emphasized that the purpose of Tucker *et al.*⁶⁵ was to determine the amounts of different species, whereas our purpose was to determine the species and bonds of different types. There need not be essential discrepancies between the two discussions, especially as in our opinion the absorptions of possible linear trimers are masked by absorptions of dimer and/or cyclic trimer associates (p. 919).

Berman⁶⁷ measured the heat capacities of six alcohols in the vapour phase. On the basis of his results and literature data he drew conclusions that are in complete agreement with ours, *viz.*, that relatively simple ordinary alcohols exist as both cyclic and linear dimers in both the vapour and liquid phases, and that the higher associates (most probably tetramers) are cyclic.

A number of recent papers have dealt with the theoretical interpretation of hydrogen bond formation by water and alcohols. These papers have been reviewed by Winde.⁶⁸

Almost all authors have concluded that the most stable structure of the water dimer is the linear one, the estimated energies of dimerization varying between -4.4 and $-12.4\text{ kcal mol}^{-1}$, in most cases between -6 and -7 kcal mol^{-1} (see Ref. 69 for a discussion of the intermolecular forces in water vapour and Ref. 70 for experimental data on the complexes of water in inert organic solvents and in the vapour phase). It is interesting to note, however, that Kollman and Allen⁷¹ found that the cyclic structure is only 1.3 kcal mol^{-1}

less stable than the linear structure. In recent papers, Diercksen⁷² estimated the bond energy of the linear water dimer to be -8.84 kcal mol⁻¹ and Hankins *et al.*⁷³ -4.72 kcal mol⁻¹.

The calculations give similar results for methanol dimers as for water dimers, *i.e.*, the linear dimers should be the most stable, the bond energy being $6-7$ kcal mol⁻¹. We cannot, however, agree with the view⁶⁸ that a cyclic structure (at least in dilute solutions in inert solvents) can be excluded on theoretical grounds, but rather accept the view of Hoyland and Kier,⁷⁴ who, although they favoured the linear form, stated that "the evidence against the cyclic dimer is far from conclusive".

Almost all calculations relating to associates of water and methanol larger than the dimer have led to the result that the cyclic form (trimer or, preferably, tetramer) is more stable than the linear form⁶⁸ (*cf.* Refs. 75 and 76).

Also the results obtained by NMR spectrometry are contradictory⁵⁴ (*cf.* Refs. 25 and 77). The NMR data do not permit a decision as to whether the alcohol dimers are cyclic or not. Dilution shifts for fluoroalcohol-benzene mixtures will be reported later.⁷⁸

We propose the association model with both cyclic and linear dimers also for phenols^{19,27,56} and silanols,⁷⁹ as the spectroscopic data for these compounds are quite similar to those for alkanols.

Practical questions concerning near-IR studies of self-association in CCl₄. First it should be mentioned that Fletcher and Heller²³ maintained that the considerable temperature dependence of the molar absorption coefficients ϵ of alcohol monomers is due to experimental errors (*cf.* Ref. 7). We are (and were also previously;² (*cf.* Ref. 4)) well aware of the fact that the great volatility of monomeric alcohols may lead to considerable errors in measured values of ϵ . We do not, however, believe that this is the main reason for the temperature variation of the molar absorption coefficients ϵ_m° of fluoroalcohol monomers at infinite dilution; in our measurements the air space was very small, and the measurements were made by cycling, *i.e.*, recordings were carried out at 25° both at the beginning and at the end of each series (*cf.* Experimental); this was the case also in the earlier work² criticized by Fletcher and Heller.²³ The recent work of Hoover *et al.*^{80a} shows unequivocally that evaporation is not the major cause of the variation of the molar absorption coefficient of an alcohol with temperature. It may be mentioned that values of ϵ_m° for TFE in the fundamental and the overtone OH stretching regions vary considerably with temperature,² whereas the value for HFP in the overtone region is constant within experimental error.² The same difference is noted also with fluorinated *t*-butyl alcohols; ϵ_m° for TFTB (fundamental vibration) varies somewhat with temperature but that for HFTB (overtone) varies only slightly (Table 1).

It is well known that carbon tetrachloride is not so "inert" a solvent for hydrogen bonding studies as would be desired; this is because of the existence of OH...Cl interactions (see the references cited by Fletcher;⁸⁰ for OH...Cl interactions between phenols and 1,1,1-trichloroethane, see Ref. 81). We accept the view that the usually observed variations of ϵ with temperature may, at least partly (perhaps even solely), arise from the OH...Cl interactions. This would also be in agreement with the independence of ϵ_m° on temperature in the case of HFP. We have proposed for HFP in dilute solution in carbon

tetrachloride two conformations arising from intramolecular interactions of the OH group with the fluorine atoms.³ If the intramolecular interactions are stronger than the interactions with the solvent, ϵ_m° should be almost independent of temperature, as has been experimentally found.² The same would apply in the case of HFTB. The variation of ϵ_m° with temperature in the case of TFE and TFTB may be due to interactions of "free" OH groups with solvent.

The OH...Cl interactions may affect the experimental results for self-association in alcohol-carbon tetrachloride mixtures. Fletcher⁸⁰ has stated that "previous hydrogen bond equilibrium studies involving OH groups in CCl₄ are in serious error". The opinion of Fletcher has been both criticized⁸² and supported.⁸³ We do not take a stand in this question, but the very complicated nature⁸⁴ of the OH stretching overtones (Fletcher studied the first overtone region) and the additional complicating factors due to the CH stretching⁸⁴ make us somewhat sceptical about the use of the region at about 1.4 μm in association studies with hydrocarbons as solvents (the most thorough studies on the first overtones of the OH stretching frequencies of alcohols are those of Luck⁸⁵ (*cf.* Ref. 86)). The spectra of TB, HFTB, and TFTB in the first overtone region are reproduced in Figs. 6-8. The decrease of the

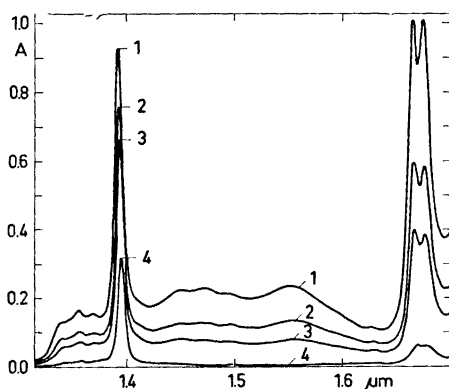


Fig. 6. Illustrative spectra of 2-methyl-2-propanol (first overtone) in CCl₄ at 25°. Molar concentrations (cell thicknesses in mm in parentheses): 1, 2.69 (10); 2, 1.62 (10); 3, 1.078 (10); 4, 0.030 (50).

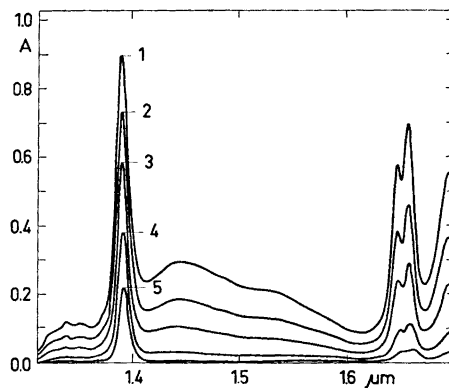


Fig. 7. Illustrative spectra of 2-trifluoromethyl-2-propanol (first overtone) in CCl₄ at 25°. Molar concentrations (cell thicknesses in mm in parentheses): 1, 4.74 (5); 2, 3.13 (5); 3, 1.98 (5); 4, 0.791 (5); 5, 0.297 (5).

absorption at about 1.56 μm with increasing fluorine substitution is seen clearly in the spectra. The monomer absorption band of HFTB at 1.4 μm is almost symmetric and no shoulder is seen. (It may be mentioned that in the case of HFP,² which gives two clearly separated maxima in the fundamental region, the maxima are less well separated in the overtone region.)

On the other hand, non-spectroscopic methods indicate that the influence of carbon tetrachloride on thermodynamic quantities is by no means very

marked. Thus, for example, Wolff and Höppel⁸⁷ found, using the vapour pressure method, that the association energy of methanol is smaller by 0.5–1.0 kcal mol⁻¹ in carbon tetrachloride (5.0–5.9 kcal mol⁻¹) than in hexane. It should also be noted that the values of $\Delta\nu(\text{dim})$ and $\Delta\nu(\text{pol})$ are of the same order of magnitude in CCl₄ as in cyclohexane.⁸⁸ We agree that carbon tetrachloride is by no means an ideal solvent for hydrogen bonding studies, but it is difficult to find a better alternative suitable for spectrometric work. In fact, only by investigating association in the vapour phase can the complicating effects of the solvent be entirely avoided.

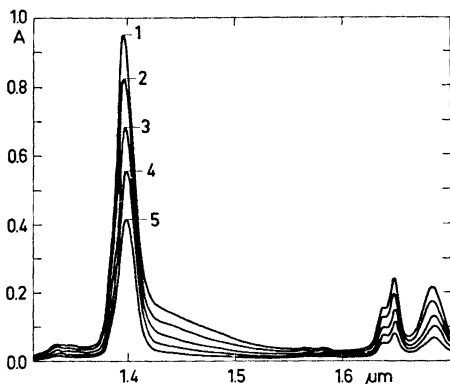


Fig. 8. Illustrative spectra of 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol (first overtone) in CCl₄ at 25°. Molar concentrations (cell thicknesses in mm in parentheses): 1, 2.67 (5); 2, 2.13 (5); 3, 1.60 (5); 4, 1.20 (5); 5, 0.799 (5).

The primary question in the spectrometric determination of thermodynamic quantities associated with the formation of alcohol dimers is whether the cyclic dimers are the only species present in dilute solutions or whether also a certain proportion of linear dimers is simultaneously present; in the latter case the absorption of the free OH groups of the linear dimers would influence the monomer absorption and lead to erroneous results. The present state of knowledge does not allow a choice between these two alternatives; the situation may also vary from alcohol to alcohol. Thus the ΔH values determined by the near-infrared method cannot always be considered very reliable (they may be apparent values influenced by the linear dimer – cyclic dimer equilibria).

Some reservations must be made concerning the discussion presented above. Firstly, it would be possible to assign the absorption shifts 90–110 cm⁻¹ to the linear and the shifts 150–160 cm⁻¹ to the cyclic dimers. (This would be permissible in the light of the Kirkwood-Fröhlich g values mentioned above, as g approaches unity at infinite dilution and this does not permit any estimate of the limiting value of g for dimers at infinite dilution). Results of some other workers (*e.g.*, Refs. 26, 89 and 90) support this explanation, but we do not, however, find it very attractive.

Secondly, one could assume that the dimers are only cyclic. Then the $\Delta\nu$ (150–160 cm⁻¹) absorption shifts would be due either to the solvent dependence of $\Delta\nu(\text{dim})$ or to larger linear associates than dimers. We find also these explanations unlikely. (The latter assumption would invalidate the

generally accepted view that the absence of $\Delta\nu$ values greater than about 160 cm^{-1} indicates that dimers are the largest associates present.)

In the above discussion we have not tried to estimate the relative abundances of the different associates (see, *e.g.*, Refs. 91–93 in addition to the references given above) because it is probable that the terminal hydroxyls of linear associates increase the monomer absorption by an indefinite amount. Especially in the case of fluoroalcohols we must also consider the possibility of bonding of a free OH group to the oxygen atom of an intramolecularly bonded hydroxyl group. Structures of this kind seem very probable to us, but as such propositions are very tentative at present, we will not discuss these further in this connection.

Recently, Farnham⁹⁴ published an interesting and extensive study on the association of TFE and HFP in the vapour phase and in hexadecane. He stressed the importance of trimers in the association of these alcohols.

CONCLUSIONS

From the experimentally determined concentration dependence of the dimer shifts we draw the following conclusions concerning the self-association of alcohols in carbon tetrachloride at temperatures near room temperature.

1. Cyclic dimers are the alcohol associates present (in addition to monomers) in the most dilute solutions. These cause a shift of about $90\text{--}110\text{ cm}^{-1}$ in the fundamental OH stretching frequency.

2. Increase of the alcohol concentration causes a gradual transition towards linear dimers with a frequency shift of about $150\text{--}160\text{ cm}^{-1}$.

3. It is possible that linear dimers are present in addition to cyclic dimers also in dilute solutions.

4. It is possible that also linear trimers or higher linear associates exist at higher alcohol contents. We tentatively ascribe shifts of $200\text{--}220\text{ cm}^{-1}$ to these. This absorption is difficult to identify in solution spectra because of the strong masking by cyclic aggregates (item 5).

5. Cyclic species dominate in moderately concentrated solutions in carbon tetrachloride and also in neat alcohols, trimers and tetramers being the most probable species (some evidence, however, points to cyclic hexamers). The corresponding shifts would be $240\text{--}300\text{ cm}^{-1}$.

6. Tentatively, we estimate the bond energies per hydrogen bond to be $2\text{--}3\text{ kcal mol}^{-1}$ for the cyclic dimers, $4.0\text{--}4.5\text{ kcal mol}^{-1}$ for linear dimers, and about 6 kcal mol^{-1} for higher cyclic species. In addition, we propose bond energies per hydrogen bond of the order of $4.5\text{--}5.0\text{ kcal mol}^{-1}$ for linear associates higher than dimers (if present).

7. This general scheme seems to hold for simple alcohols, for highly branched alcohols (in these cases dimers may be practically the only associates), and for halogenated alcohols.

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