362. *Studies in Spectroscopy. Part II.* The Ionisation Constants and Infra-red Spectra of Some Primary and Secondary Halogen-containing Alcohols.*

By R. N. HASZELDINE.

The primary alcohols $R{\cdot}CH_2{\cdot}OH$ (R = perfluoroalkyl, $CHF_2{\cdot}CF_2$, $CHF_2{\cdot}[CF_2]_3$, CHF_2, CF_2Cl or CCl_3) and the secondary alcohols $CHRR'{\cdot}OH$ (R = perfluoroalkyl, R′ = alkyl) have ionisation constants some 10^4 greater than their hydrocarbon analogues. When both R and R′ are perfluoroalkyl a further 10-fold increase in acidity is observed. The infra-red spectra of these alcohols, and of certain chlorine-containing alcohols, in the 3-μ region reveal the effect of hydrogen bonding. Intermolecular hydrogen bonding is much reduced and is almost non-existent in the secondary polyhalogeno-alcohols; intramolecular hydrogen bonding of the $O{-}H{\cdots}X$ type is considered.

THE synthesis of perfluoro-*sec.*-alcohols (preceding paper) enables the effect of introducing halogen, particularly fluorine, into primary and secondary aliphatic alcohols on ionisation constants and hydrogen bonding to be measured.

The ionisation constants of a series of primary and secondary alcohols are recorded in Table 1. It is emphasised that the figures are not absolute values suitable for quantitative comparison with those obtained in aqueous solution, and that they are open to the errors outlined in the Experimental section. They serve, however, to compare the acid strengths of the various alcohols against each other in the particular solvent used (50% aqueous ethanol).

For the primary alcohols, comparison of ethanol (R = Me; $K = 3 \times 10^{-16}$; Denner and Hildebrand, *J. Amer. Chem. Soc.*, 1922, **44**, 2824) with trifluoroethanol shows that replacement of hydrogen by fluorine causes an increase in acidity in the ratio of $\sim 10^4$, in agreement with investigations by McBee, Marzluff, and Pierce (*ibid.*, 1952, **74**, 444), and

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* Part I, *J.*, 1952, 3284.

Henne and Pelley (*ibid.*, p. 1426) (cf. Swarts, *Bull. Soc. chim. Belg.*, 1929, **38**, 99, who reported $K = 10^{-7}$).

The trifluoromethyl group contains three electronegative fluorine atoms bound to carbon and should, if the inductive effect is all-important, be more electron-attracting than, say, C_2F_5 or C_3F_7 formed by replacement of a fluorine atom by a less electronegative perfluoroalkyl group. On this basis one would predict that trifluoroacetic acid is an acid appreciably stronger than pentafluoropropionic acid, and that little difference in acid strength will be detected (by refined technique in non-aqueous media) in the series $R_F{\cdot}CO_2H$ ($R_F = C_2F_5$, C_3F_7, C_4F_9, etc.), since although passage from pentafluoropropionic to heptafluorobutyric acid also involves replacement of a fluorine atom by a less electronegative trifluoromethyl group, the difficultly polarised CF_2 group adjacent to the carbonyl group will effectively shield changes in the β-position. It can similarly be predicted that the alcohol $R{\cdot}CH_2{\cdot}OH$ where $R = CF_3$ would be a stronger acid than that with $R = C_2F_5$, and that little change should be apparent for $R = C_3F_7$, C_4F_9, etc., or for $R = R'{\cdot}CF_2{\cdot}CF_2$, where R′ is a group not necessarily containing fluorine. The accuracy of the method used for the determination of K is such that only a value $4—5 \times 10^{-12}$ can be given for alcohols where $R = R'{\cdot}CF_2{\cdot}CF_2$, but there is some indication that K is higher when $R = CF_3$ than in the other examples (see also the secondary alcohols).

TABLE 1. *Approximate* pK_a *values of primary alcohols,* $R{\cdot}CH_2{\cdot}OH$, *and secondary alcohols,* in* 50% *alcohol.*

R	CF_3	C_2F_5	C_3F_7	C_4F_9	C_5F_{11}	C_7F_{15}	CCl_3
pK_a …………	11·32	11·35	11·36	11·35	11·37	11·35	11·80
$10^{12}K$ …………	$4\cdot_8$	$4\cdot_5$	$4\cdot_4$	$4\cdot_5$	$4\cdot_3$	$4\cdot_5$	$1\cdot_6$

R	CHF_2	CF_2Cl	$CHF_2{\cdot}CF_2$	$CHF_2{\cdot}CF_2]_3$	$CF_3{\cdot}CH_2$	$CF_3{\cdot}[CH_2]_2$
pK_a …………	12·00	11·62	11·34	11·35	12·7	12·9
$10^{12}K$ …………	$1\cdot_0$	$2\cdot_4$	$4\cdot_6$	$4\cdot_5$	0·2 †	0·1 †

	$CF_3{\cdot}CHMe{\cdot}OH$	$C_3F_7{\cdot}CHMe{\cdot}OH$	$C_3F_7{\cdot}CHEt{\cdot}OH$	$C_3F_7{\cdot}CHPr{\cdot}OH$
pK_a …………	11·28	11·38	11·37	11·37
$10^{12}K$ …………	$5\cdot_2$	$4\cdot_2$	$4\cdot_3$	$4\cdot_3$

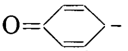
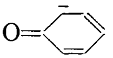
	$C_3F_7{\cdot}CH(CF_3){\cdot}OH$	$C_3F_7{\cdot}CH(C_2F_5){\cdot}OH$	$(C_3F_7)_2CH{\cdot}OH$
pK_a …………	10·46	10·48	10·52
$10^{12}K$ …………	35	33	30

* Values for secondary alcohols presented at the Amer. Chem. Soc. Meeting, Atlantic City, September, 1952.

† These values are probably high; see below.

The pK_a values for $CF_3{\cdot}[CH_2]_2{\cdot}OH$ and $CF_3{\cdot}[CH_2]_3{\cdot}OH$ are probably appreciably higher than recorded in Table 1, since the experimental method becomes insensitive in this region. The results, however, show the marked decrease in K on changing from $CF_3{\cdot}CH_2{\cdot}OH$ to $CF_3{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH$, and this is attributed to the large difference in inductive effect between a CF_3 group and a $CF_3{\cdot}CH_2$ or $CF_3{\cdot}[CH_2]_2$ group (cf. $CF_3{\cdot}CO_2H$, $CF_3{\cdot}CH_2{\cdot}CO_2H$, $CF_3{\cdot}[CH_2]_2{\cdot}CO_2H$; Henne and Fox, *J. Amer. Chem. Soc.*, 1951, **73**, 2323).

The values of K for primary alcohols where $R = CCl_3$, CHF_2, and CF_2Cl are comparable and, as expected, are appreciably less than when R = perfluoroalkyl. It is noteworthy that trifluoroethanol is not more than ten times more acidic than trichloroethanol.

In secondary alcohols containing only one perfluoroalkyl group, $K = 4—5 \times 10^{-12}$, as for the primary alcohols, and the inductive effect of the perfluoroalkyl group far outweighs that of the opposing alkyl group. Introduction of a second perfluoroalkyl group causes a marked increase in acid strength, however, with $K = 3 \times 10^{-11}$, although the effect is only one-thousandth of that caused by introduction of the first perfluoroalkyl group into methanol. The value of K for the secondary perfluoro-alcohols agrees with their failure to liberate carbon dioxide from sodium carbonate solution (*i.e.*, $K < 10^{-10}$), although they are much more soluble in dilute sodium hydroxide solution than in water. It thus appears that maximum polarisation of the OH group is almost achieved by introduction of the first perfluoroalkyl group, and the ionisation constant of a tertiary perfluoro-alcohol should thus be only slightly larger than that of a secondary one. Results will be presented later to show that this is so. An important factor here is the absence of important resonance stabilisation of the secondary perfluoro-alkoxide ion which could cause spread of the charge from oxygen; thus, the inductive effect of an R_2CH (R = perfluoroalkyl) group is greater than that for phenyl, yet phenol ($K = 1 \times 10^{-10}$) is comparable in acidity with the secondary perfluoro-alcohols, since resonance effects involving structures of the ion such as  or  lead to greater ionisation. A perfluorophenol, where both inductive and resonance effects can operate, should thus be much stronger than phenol.

The lower basicity of the oxygen atom with increasing fluorine content of the molecule is shown by boiling-point and infra-red measurements. Table 2 indicates that intermolecular hydrogen bonding decreases with increase in fluorine content of a secondary alcohol.

TABLE 2. *B. p.s of* CHRR′·OH.

R	Pr	Pr	Pr	C_3F_7	C_3F_7	C_3F_7	C_3F_7	C_3F_7	C_3F_7
R′	Me	Et	Pr	Me	Et	Pr	CF_3	C_2F_5	C_3F_7
B. p.	119	135	155	101	114	128	50/210 mm.	61/150 mm.	70/103 mm.

The solubility of secondary perfluoro-alcohols in water or concentrated sulphuric acid decreases with increase in molecular weight, as it does for perfluoro-carboxylic acids, and perfluorohexan-3-ol is substantially insoluble in these solvents.

It is well established that the vapour of an alcohol, or dilute solutions of the alcohol in a solvent such as carbon tetrachloride, show a sharp infra-red absorption band at *ca.* 2·75 μ which is characteristic of the non-hydrogen-bonded hydroxyl group ("free" hydroxyl group), and that an alcohol in the pure liquid or solid state, or in concentrated solution in carbon tetrachloride, will show a broad band at *ca.* 3 μ characteristic of the intermolecularly hydrogen-bonded hydroxyl group ("bonded" hydroxyl group) (see, *e.g.*, Fox and Martin, *Proc. Roy. Soc.*, 1937, *A*, **162**, 419). The infra-red spectra of the series of halogen-containing alcohols have therefore been investigated in the 1—4-μ region in solution and in the pure state, and provide qualitative information of the extent of hydrogen-bonding.

Intermolecular Hydrogen Bonding.—The wave-lengths of the bands under discussion are shown in Table 3. Data for ethyl and *iso*propyl alcohol are included for comparison. The spectra are of three main types, shown in Figs. I—III.

The liquid polyfluoro-alcohols $R{\cdot}CH_2{\cdot}OH$ ($R = CF_3$, C_2F_5, C_3F_7, $CHF_2{\cdot}CF_2$, $CHF_2{\cdot}[CF_2]_3$, CHF_2) show similar spectra which closely resemble those of unsubstituted alcohols, with a broad, strong band of the bonded-OH group near 3 μ (Fig. I*a*). Some indication of reduced hydrogen bonding relatively to unsubstituted alcohols is given by the weak but definite free-OH peak at *ca.* 2·75 μ on the side of the bonded OH band, since unsubstituted alcohols show only a very slight inflection at this point. When $R = CHF_2$ or $CF_3{\cdot}CH_2$, the 2·75-μ band appears as a pronounced inflection. The bonded-OH band is much reduced in intensity when the primary polyfluoro-alcohols are dissolved in carbon tetrachloride and is shifted to 2·87—2·91 μ; the free-OH band at 2·77—2·78 μ is sharp and its intensity relative to the bonded-OH group increases with increasing dilution, until finally the bonded-OH group disappears. The OH overtone band appears at 1·49 μ (Figs. I*b*, *c*, and *d*).

By using comparable concentrations (0·05—0·1M) of the alcohols in which R = Et, CF_3, and $CHF_2{\cdot}CF_2$, a difference in hydrogen bonding can be detected, since the relative intensity of the bonded-OH band to the free-OH band is less when $R = CF_3$ or $CHF_2{\cdot}CF_2$ than when R = Et.* The concentrations used are limited by the low solubility of the fluoro-alcohols in carbon tetrachloride, so that comparisons have to be made when the bonded-OH band has only a moderate intensity (Fig. I*c*). The decrease in intermolecular hydrogen bonding is, however, more effectively shown by comparison of ethanol and trichloroethanol, since the latter is readily soluble in carbon tetrachloride. At 0·2M concentration ethanol has a spectrum of contour Fig. I*b*, *i.e.*, the bonded-OH group

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* A Referee has kindly pointed out that this assumes that halogen substitution in the alcohol has much the same effect on the extinction coefficients of the two bands.

predominates, but with identical concentration trichloroethanol has spectrum Fig. 1*c* *i.e.*, the free-OH group predominates. Pure trichloroethanol shows an inflection at 2·75 μ, with the bonded-OH band at 3·03 μ.

The ultra-violet spectroscopic results (Table 4) are of interest in connection with the basicity of oxygen in polyhalogeno-alcohols.

Kleinberg and Davidson (*Chem. Reviews*, 1948, **42**, 601) quote literature values of 480 mμ for a solution of iodine in EtOH and 540 mμ for that in CCl_4. Benesi and

TABLE 3. *Infra-red spectra of halogenated alcohols in the* 1—4-μ *region.*

(a) *Primary alcohols*, $R\cdot CH_2\cdot OH$.

	Pure compound.		CCl$_4$ solutions.		
			Conc. solution.		Effect of dilution
R	Bonded OH	Free OH	Bonded OH	Free OH	
CF_3 [1]	2·99 (b.s.)	2·77 (w.si)	2·87 (b.m.)	2·77 (sh.s.) 1·49 (sh.vw.)	Bonded OH band vanishes on high dilution
C_2F_5 [1]	2·99 (b.s.)	2·78 (w.si)	2·88 (b.m.)	2·78 (sh.s.) 1·49 (sh.vw.)	
C_3F_7 [1]	3·00 (b.s.)	2·79 (w.si)	2·89 (b.m.)	2·78 (sh.s.) 1·49 (sh.vw.)	
$CHF_2\cdot CF_2$ [1]	3·03 (b.s.)	2·8 (w.si)	2·88 (b.m.)	2·77 (sh.s.) 1·49 (sh.vw.)	
$CHF_2\cdot[CF_2]_3$ [1]	3·01 (b.s.)	2·75 (w.si)	2·91 (b.m.)	2·78 (sh.s.) 1·49 (sh.vw.)	
CHF_2 [2]	3·02 (b.s.)	2·75 (infl.)	3·0 (b.s.)	2·78 (sh.m.) 1·49 (sh.vw.)	
$CF_3\cdot CH_2$ [2]	3·02 (b.s.)	2·75 (infl.)	3·0 (b.s.)	2·78 (sh.m.) 1·49 (sh.vw.)	
CCl_3 [3]	3·03 (b.s.)	2·75 (infl.)	2·91 (b.s.)	2·80 (sh.s.) 1·49 (sh.vw.)	Bonded OH 2·87 and disappears on dilution. Free OH 2·78
$CH_3\cdot CH_2$	3·01 (b.s.)	—	3·0 (b.s.)	2·75 (sh.m.) 1·46 (sh.vw.)	Bonded OH vanishes on high dilution

(b) *Secondary alcohols.*

	Pure compound		CCl$_4$ solutions		
			Conc. solution		Effect of dilution
Alcohol	Bonded OH	Free OH	Bonded OH	Free OH	
$CF_3\cdot CHMe\cdot OH$ [1]	2·98 (b.s.)	2·8 (w.infl.)	2·92 (b.m.)	2·76 (sh.s.) 1·47 (sh.vw.)	Bonded OH band vanishes
$C_3F_7\cdot CHMe\cdot OH$ [2]	2·98 (b.s.)	2·8 (w.infl.)	2·29 (b.m.)	2·77 (sh.s.) 1·47 (sh.vw.)	
$C_3F_7\cdot CHPr\cdot OH$ [2]	2·98 (b.s.)	2·79 (w.infl.)	2·91 (b.m.)	2·78 (sh.s.) 1·49 (sh.vw.)	
Pr^iOH	3·01 (b.s.)	—	3·00 (b.s.)	2·75 (sh.m.) 1·46 (sh.vw.)	
$(CCl_3)_2CH\cdot OH$ [3]	2·9 (s.)	2·82 (sh.s.)	—	2·79, 2·83 (sh.s. doublet) 1·50 (sh.vw.)	No change in relative intensity
$CCl_3\cdot CH(C_2Cl_5)\cdot OH$ [3]	2·95 (s.)	2·86 (sh.s.)	—	2·80, 2·85 (sh.s. doublet) 1·5 (sh.vw.)	
$C_3F_7\cdot CH(C_2F_5)\cdot OH$ [1]	2·90 (m.)	2·78 (sh.s.)	—	2·76 (w.si.) 2·79 (sh.s.) 1·5 (sh.vw.)	No change in relative intensity
$(C_3F_7)_2CH\cdot OH$ [1]	2·89 (m.)	2·79 (sh.s.)	—	2·76 (w.si) 2·79 (sh.s.) 1·5 (sh.vw.)	

[1] Low solubility in CCl_4. [2] Moderate solubility in CCl_4. [3] Very soluble in CCl_4.

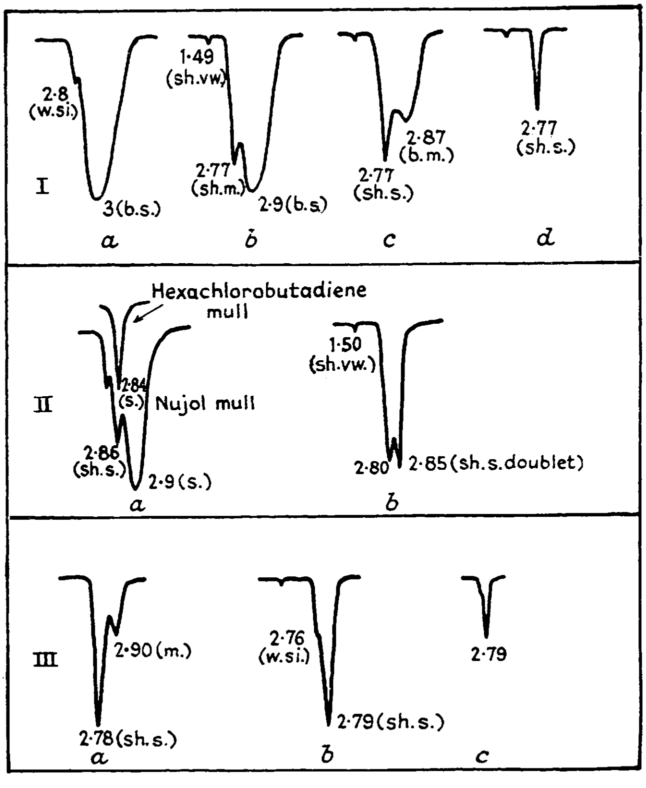
b. = broad; infl. = inflection; m. = medium; s. = strong; sh. = sharp; si. = side-band; vw. = very weak; w. = weak.

TABLE 4. *Ultra-violet spectra of iodine in various solvents.*

Solvent	EtOH	$CHF_2\cdot CF_2\cdot CH_2\cdot OH$	$CCl_3\cdot CH_2\cdot OH$	CCl_4
$\lambda_{max.}$, mμ	444	490	500	516

Hildebrand (*J. Amer. Chem. Soc.*, 1949, **71**, 2703) report 517 mμ for CCl_4 solutions. Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 600) attributed the shift in maximum from carbon tetrachloride to ethanol solutions to complex formation of the acid–base type in which iodine acts as an electron-acceptor, and an electron of the lone pair of the oxygen atom is partly transferred to the iodine. The long-wave-length maximum for iodine in the alcohols where R = CCl_3 or $CHF_2{\cdot}CF_2$ is displaced to the visible region relatively to that in ethanol, as would be expected for decreased basicity of oxygen. The solution of iodine in the chloro-alcohol unexpectedly resembles that in carbon tetrachloride more than does that in the fluoro-alcohol; this is possibly correlated with the much higher solubility of iodine in a polychloro-compound such as carbon tetrachloride than in a polyfluoro-compound such as a fluorocarbon, or it may indicate steric hindrance of complex formation in the chloro-alcohol.

Infra-red spectra of halogeno-alcohols in the 3-*μ region.*



(*a*) *Pure compound.* (*b, c, d*) CCl_4 *solutions of decreasing concentration. See footnotes to Table* 3 *for abbreviations.*

In assessing the change in intermolecular hydrogen bonding on introduction of halogen into an alcohol, two opposing factors are involved: reduction in the basicity of the oxygen atom will reduce the strength of the hydrogen bond in which this oxygen acts as electron donor, but the increase in acidity of the alcohol revealed by the ionisation constant data, *i.e.*, increases in the effective positive charge on the hydrogen atom, will lead to an increase in the strength of the hydrogen bond in which the acidic hydrogen atom participates. The first of these effects apparently predominates in the primary polyhalogeno-alcohols, since intermolecular hydrogen bonding is reduced relatively to that in the hydrocarbon analogues.

The secondary alcohols R·CH(OH)Alkyl (R = perfluoroalkyl) show a free-OH band at 2·8 μ (inflection) in their infra-red spectra, but the bonded-OH band still predominates

(Fig. I*a*); the spectra in solution are similar to those of the primary halogen-containing alcohols (Fig. I*b*—*d*), and indicate reduced hydrogen bonding relatively to that in *iso*propyl alcohol.

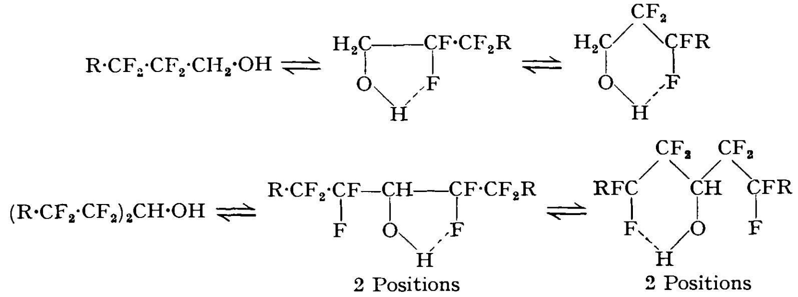
The secondary polyhalogeno-alcohols show a marked change. 1 : 1 : 1 : 3 : 3 : 3-Hexachloropropan-2-ol in Nujol suspension shows a strong band at 2·9 μ which is much sharper than that normally observed for the bonded-OH group; 1 : 1 : 1 : 3 : 3 : 4 : 4 : 4-octachlorobutan-2-ol similarly shows a band at 2·95 μ with a free-OH band at 2·86 μ (Fig. II*a*). The intermolecular hydrogen bonding is extremely weak, since, even though the alcohols are readily soluble in carbon tetrachloride, the most concentrated solution fails to show a band in the 2·9—3·0-μ region. That the weak intermolecular hydrogen bonds are broken as soon as the alcohols dissolve is also shown by use of hexachlorobutadiene as suspending medium instead of Nujol, since the alcohols partly dissolve in the chloro-diene and only a strong band at 2·84 μ is shown in the spectrum (Fig. II*a*). The possible significance of the doublet in the 2·79—2·85-μ region of the spectrum for carbon tetrachloride solutions (Fig. II*b*) is discussed below.

The secondary perfluoro-alcohols also differ markedly from the alkylperfluoroalkylcarbinols. In the pure liquids the band attributed to the free-OH group (2·78 μ) is very strong and that at 2·9 μ is only weak (Fig. III*a*); the latter band is sharper than for the usual bonded-OH group. Intermolecular bonding is thus very weak, and it is noteworthy that the change with the perfluoro-alcohols, where the ionisation constant has been increased only 10-fold relatively to that for primary fluoro-alcohols, is much greater than that observed for the latter compared with the unsubstituted alcohols, for which a change in ionisation constant of 10^4 is involved. Fluorine is only slightly larger than hydrogen, so steric factors are probably not important in the secondary perfluoro-alcohols, although steric inhibition of intermolecular hydrogen bonding may be involved in the chloro-alcohols.

In solution (limited by the solubility) no band attributed to a bonded-OH group can be observed in the spectra of secondary perfluoro-alcohols, and the free-OH band at 2·79 μ with a weak side band at 2·76 μ is not changed in position or relative intensity by subsequent dilution (Fig. III*b* and *c*).

The bonded-OH vibration in the pure compounds recorded in Table 3 shows a distinct trend to shorter wave-length relatively to that for unsubstituted alcohols, also indicating reduced intermolecular hydrogen bonding, particularly in the secondary polyhalogeno-alcohols.

Intramolecular Hydrogen Bonding.—In the above discussion, a band at *ca.* 2·75—2·80 μ has been ascribed to a " free OH group." The hydroxyl group producing a band at this position in unsubstituted alcohols is clearly " free," but in the halogeno-alcohols intramolecular hydrogen bonding of the O–H---F or O–H---X type is possible, with formation of five- or six-membered rings:



The evidence at present available suggests that hydrogen bonding of this type can occur in the polyhalogeno-alcohols but is not strong. The " free "-hydroxyl bands observed in carbon tetrachloride solutions are at slightly longer wave-lengths (2·77—2·79 μ) than those observed in parallel experiments with solutions of unsubstituted alcohols (EtOH, 2·75; Pr^{i}OH, 2·75; Bu^{t}OH, 2·76 μ). This shift is small but definite, and in absence of more detailed studies with a prism of higher resolving power may be ascribed either to the effect of the adjacent polyhalogeno-group or groups on the stretching vibration of the free hydroxyl group, or to intramolecular hydrogen bonding of the O–H---X type. If intramolecular hydrogen-bonding is occurring, then the doublet observed in the carbon tetrachloride solution spectra of the chloro-alcohols, and possibly the weak side band in the solution spectra of the secondary perfluoro-alcohols, may be significant, since the peaks at lower wave-length [$(CCl_3)_2CH\cdot OH$ 2·79, $CCl_3\cdot CH(C_2Cl_5)\cdot OH$ 2·80, $C_3F_7\cdot CH(C_2F_5)\cdot OH$ *ca.* 2·76, $(C_3F_7)_2CH\cdot OH$ *ca.* 2·76] could be ascribed to a truly free hydroxyl group and the stronger bands of the doublet (Table 3) to the O–H---X bonded hydroxyl group. The overtone hydroxyl group band is also at longer wave-length (1·49—1·50 μ) than that in hydrocarbon alcohols (1·46—1·47 μ), but the fact that it appears at all in carbon tetrachloride solution shows that the intramolecular hydrogen bonding is not strong, *i.e.*, resembles the bonding in *o*-chlorophenol rather than that in *o*-nitrophenol.

EXPERIMENTAL

Determination of Ionisation Constant.—A convenient and rapid method for determination of ionisation constant is that used by Bennett, Brooks, and Glasstone (*J.*, 1935, 1821), involving determination of pH at the half-neutralisation point and application of the Henderson equation $pH = pK_a$. This gives accurate results for the range 4—10, but for pH $>10{\cdot}5$ errors caused by hydrolysis arise (Glasstone, "Electrochemistry of Solutions," Methuen, 1945, pp. 218—222). To keep such errors as low as possible, fairly concentrated solution (0·1N) in 50% aqueous ethanol were used where possible. This solvent is convenient, since (*a*) not all the alcohols studied are sufficiently soluble in water to enable comparable concentrations to be used throughout, and (*b*) K_w for 50% aqueous ethanol will be in the range 10^{-16}—10^{-14} compared with 10^{-14} for water, and hydrolysis errors will be reduced (see equations in Glasstone, *op. cit.*).

The alcohols were mainly samples prepared in these laboratories (Haszeldine, *J.*, 1952, 3423; 1950, 2789; preceding paper; *Nature*, 1950, **166**, 192; 1951, **168**, 1028; Haszeldine and Leedham, *J.*, 1953, 1548) and stored in sealed ampoules before use. The compounds $CCl_3\cdot CHR\cdot OH$ ($R = CCl_3, C_2Cl_5$) were kindly supplied by CIBA Ltd., Switzerland (see Geiger, Usteri, and Granacher, *Helv. Chim. Acta*, 1951, **34**, 1335). W. C. Francis and A. L. Henne have recently reported (personal communication) that K for $(C_3F_7)_2CH\cdot OH$ is $2{\cdot}2 \times 10^{-11}$.

Solutions were made up by weight, and volumetric apparatus was calibrated before use. Portions (5, 10, or 20 ml.) of the alcohol solution were titrated against carbonate-free 0·1N-sodium hydroxide in the same solvent. The pH at the half-neutralisation point was measured by a Cambridge Instrument Co. meter fitted with an Alki-Glass or Doran sealed-glass electrode for the pH range 10—13, and standardised against a series of buffers. Two determinations were made with each alcohol. A control experiment with phenol gave $K = 0{\cdot}8 \times 10^{-10}$ in water (lit., 1×10^{-10}), and $K = 0{\cdot}4 \times 10^{-10}$ in 50% aqueous ethanol. Bennett *et al.* (*loc. cit.*) have shown that the order of strengths of a series of weak acids is the same in 30% aqueous ethanol as in water, although the pK values are 0·3—0·5 unit higher than in water.

The accuracy of the results summarised in Table 1 is probably $\not> 0{\cdot}5 \times 10^{-12}$ for ionisation constants 1—10×10^{12}, with a somewhat greater accuracy for the secondary perfluoro-alcohols. The method is insensitive for $K < 1 \times 10^{-12}$, and results in this region are probably high.

Infra-red Spectra.—A Perkin–Elmer Model 21 Double Beam Instrument with sodium chloride optics was used. Wave-lengths are accurate to ±0·01 μ. The spectra of the pure compounds were examined either as a liquid film (0·025 mm. thick), or as a suspension in Nujol or hexachlorobutadiene. Moisture was carefully excluded. The spectra of carbon tetrachloride solutions were taken in 1·0- or 3·0-mm. cells. Solutions were made up approximately, at concentrations from 0·05 to 0·5M depending on solubility, or, if a compound was only slightly soluble, a saturated solution was used. Dilutions were made from the parent solutions.

Ultra-violet spectra were determined on a Unicam Spectrometer, 1-cm. silica cells being used.

Grateful acknowledgment is made to CIBA Ltd., Switzerland, for the gift of two of the compounds used in this investigation.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, December 16th, 1952.*]