PROTON DONOR AND PROTON ACCEPTOR ABILITY OF SOME ALCOHOLS IN TETRACHLOROMETHANE AND INTRAMOLECULAR INTERACTION IN SILYL- AND GERMYLALKANOLS*

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Proton acceptor and proton donor abilities of some alcohols ROH in CCl_4 were measured by IR spectroscopy. Both properties are explained in terms of solvent effect and the electronic effect of group R. The earlier proposed intramolecular interaction in the alcohols $R_3M(C)_nOH$ (M = Si, Ge; $n = 1,2$) is further discussed.

Characteristic features of oxygen-containing carbofunctional compounds of group IV B elements (M) have been frequently interpreted in terms of the electron donor effect of R_3MCH_2-groups and the electron acceptor ability of the atom M. Reactivity of the alcohols $(CH_3)_3M(CH_2)_nOH$ ($n = 1,2$) toward electron acceptors[1-3] is consistent with the electron-donating effect of $(CH_3)_3$. $M(CH_2)_n$-groups. The structure of the compounds $(C_6H_5)_3MCH_2OH$ and $2\text{-}(C_6H_5)_3M$. $C_6H_{10}OH$ (M = Si, Ge) was however interpreted by means of IR spectroscopy in terms of the $(p-d)\,\sigma$ interaction of the oxygen with the atom M (ref.[4,5]). The existence of this interaction has been deduced[4-6] from comparison of the relative acidity of the alcohols $(C_6H_5)_3M(C)_nOH$ (M = C, Si, Ge) which was estimated from the shift of the IR absorption band of the hydroxy group of the alcohol due to its interaction with tetrahydrofuran and dimethylsulfoxide. However, the relative acidity of some phenylalkanols ($\Delta v(OH) = v(OH)_{free} - v(OH)_{assoc.}$) could not be evaluated for the following reasons. With triphenylmethylsubstituted alcohols of the type $(C_6H_5)_3C(CH_2)_nOH$ ($n = 0-2$), formation of intramolecular hydrogen bond between hydroxylic hydrogen and π-electrons of benzene ring takes place[7]; this bond is weak[7-9] in $(C_6H_5)_3COH$ and $(C_6H_5)_3C(CH_2)_2OH$ but makes it impossible to determine the accurate position of the $v(OH)$ band for both compounds. Although such intramolecular hydrogen bond has not been reported for $2\text{-}(C_6H_5)_3CC_6H_{10}OH$, the same values of the $v(OH)$ for this compound[4,5] and 2,2,2-triphenylethanol[7] ($\sim 3590\ cm^{-1}$) can be ascribed to analogous conformers *I* and *II* with strong intramolecular hydrogen bond (2-triphenylmethylcyclohexanol was prepared[5] by reaction leading to the *trans* isomer[10], the equatorial position of the triphenylmethyl group on cyclohexane is energetically favoured). There are data *(e.g.*[11-13]) which convincingly show that intramolecular hydrogen bond between hydroxyl group and the proton acceptor in position 6 is preferable to the

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interaction with proton acceptor in position 5. The stronger hydrogen bond in 2-triphenylmethyl-cyclohexanol (only the ν(OH) band at $3590\ \text{cm}^{-1}$) (ref.[4]) compared to 3,3,3-triphenylpropanol (ν(OH)$_{\text{free}}$ at $3633\ \text{cm}^{-1}$ and ν(OH)$_{\text{assoc.}}$ $3601\ \text{cm}^{-1}$) (ref.[7]) demonstrates further the effect of the rigidity of the structure. Replacement of the quarternary carbon of the compounds $(C_6H_5)_{3-n}$ $(CH_3)_nC(CH_2)_mOH$ ($m = 1,2$) by silicon leads to such weakening[14] of the hydrogen bond (this is obviously also true for the replacement of the carbon by germanium) that the ν(OH)$_{\text{free}}$ band position can be directly read. The neglection of the intramolecular hydrogen bond in the series

$(C_6H_5)_3M(\overset{|}{\underset{|}{C}})_nOH$ ($n = 1,2$) leads therefore to erroneous interpretation of the $\Delta\nu$(OH) values.

In fact, the alcohols $(C_6H_5)_3MCH_2OH$ and $2\text{-}(C_6H_5)_3MC_6H_{10}OH$ with M = Si and Ge were considered more acidic than their carbon analogues[4,5].

I   *II*
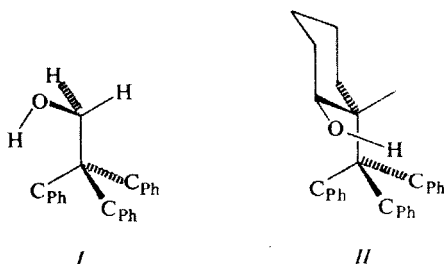
We previously investigated by IR spectroscopy the possibility of intramolecular interaction in the alcohols $(CH_3)_3M(CH_2)_nOH$ (M = Si, Ge; $n = 1,2$). In this work we consider it useful to discuss these data (IR spectra, relative basicities and relative acidities) in relation to the same properties of some other alcohols.
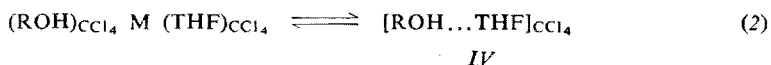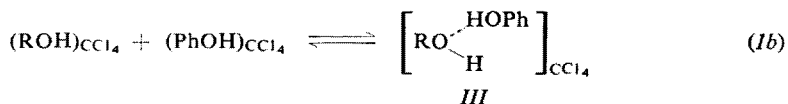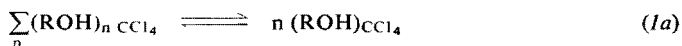
EXPERIMENTAL

Substances. 2,2-Dichloroethanol and 2,2,2-trichloroethanol were prepared by reduction of 2,2-dichloroacetyl chloride or chloral with lithium aluminium hydride. Their physical constants (Cl_2HCCH_2OH; b.p. 53°C/8 Torr, n_D^{20} 1·4668; Cl_3CCH_2OH: b.p. 60°C/20 Torr, n_D^{20} 1·4868) agreed with reported data. Preparation of the alcohols $(CH_3)_3M(CH_2)_nOH$ (M = C, Si, Ge; $n = 1,2$) was described elsewhere[1,2,15]. Methanol, ethanol, 1-propanol, 2-propanol, allyl alcohol, 1-butanol, 2-chloroethanol, phenol (all supplied by Lachema, Brno), benzyl alcohol (Sojuz-chim-export, Moscow), 2-phenylethanol, 2-bromoethanol, tert-butanol (all supplied by Fluka AG., Buchs) and 2-butanol (Reanal, Budapest) were rectified before use. Tetrahydrofuran (THF) was dried by LiAlH$_4$ and rectified. Tetrachloromethane was of spectrograde purity (both supplied by Lachema, Brno).

IR *spectra* were recorded with a double-beam Zeiss (Jena). Model UR-20 spectrophotometer in the $3100-3700\ \text{cm}^{-1}$ region (LiF prism). With the aim of evaluating the relative acidity and basicity of the hydroxy group of the alcohols, the IR spectra in the region of hydrogen bonds were measured with following systems: 0·02M phenol/0·5M alcohol/CCl$_4$ (alcohol as proton accep-

tor) and 0·02M alcohol/1M tetrahydrofuran/CCl$_4$ (alcohol as proton donor). The reference cell contained 0·5M solution of a given alcohol in CCl$_4$ and 1M solution of tetrahydrofuran in CCl$_4$, respectively. The sodium chloride cell used was 0·01 cm thick. Wavenumbers were read with an accuracy of ± 3 cm^{-1}, the $\Delta\nu$ values were taken as an average of three measurements.

RESULTS AND DISCUSSION

The order of relative basicities or acidities in liquid phase (in solvent) is analogous to the order of relative intrinsic basicities or acidities only when solvation does not affect the resonance and electrostatic effects of substituents as well as the character of „through space" intramolecular interaction between substituent and the center of acidity (basicity). In other words, solvation effects should not be more important than molecular effects. The IR spectroscopic determination of basicities (acidities) in aprotic CCl$_4$ is based on the Badger–Bauer relation[16,17] whose general applicability was questioned, but for appropriately chosen donor (acceptor) solvent systems was confirmed by Drago and collaborators $(cf.^{18-20})$. This evaluation provides cancellation of levelling effect[21], and with appropriately chosen systems it does not involve formation of ion-aggregates[22]. Equilibrium reactions (1)–(2) studied in the present work can be considered as the equilibria of isoionic acid (base), and their influencing by solvent[23] consists only in formation of collision complexes[24] of all the components present.

$$\sum_n (ROH)_{n\ CCl_4} \ \rightleftharpoons\ n\,(ROH)_{CCl_4} \tag{1a}$$

$$(ROH)_{CCl_4} + (PhOH)_{CCl_4} \ \rightleftharpoons\ \left[RO \overset{HOPh}{\underset{H}{\diagdown}} \right]_{CCl_4} \tag{1b}$$

$$III$$

$$(ROH)_{CCl_4}\ M\ (THF)_{CCl_4} \ \rightleftharpoons\ [ROH...THF]_{CCl_4} \tag{2}$$

$$IV$$

Although the conditions used in the measurements of relative acidity (basicity) (in CCl$_4$) do not prevent the alcohols from being associated, the equilibrium $(1a)$ exists between the associates and the monomer. It can be therefore assumed that only the monomer interacts with phenol, since the oxygen of n-mers is already engaged in interaction with additional molecule of the alcohol. In Table I are recorded shifts of the ν(OH) band of phenol due to its interaction with alcohols (relative basicity) and shifts of the ν(OH) band of the alcohols due to their interaction with tetrahydrofuran (relative acidity). Correlations of these quantities with various substituent constants including polar effects, are presented in Table II.

Before entering into the discussion of basicities of the alcohols, it should be noted that the methods for evaluating weak bases[35], and particularly alcohols[36], are in

amphiprotic solvents complicated by levelling effect, and in strong acids by difficulties in defining solvated species. The fact that the order of relative basicities of the oxygeneous bases in strong acids $(ROR > ROH > HOH)$, which was deduced from the correlation of the enthalpy of protonation of bases by strong acids with their pK'_As in water[37], is consistent with the order of proton affinities of the alcohols in gas phase[38] is thus very surprising. The basicities of alkanols obtained in this work by following interaction of the alcohols with phenol in CCl_4 (Table I) can be explained by prevailing electron donor effect of alkyl groups in the complex formed between the alcohol and phenol (III). Relative basicities of the alcohols $(CH_3)_3Si(CH_2)_nOH$ $(n = 1,2)$ are controlled in the same way and correlate with Taft σ^* constants (Table II, correlations 1 and 2). The electron donor effects of $(CH_3)_3MCH_2$- or $(CH_3)_3M(CH_2)_2$- $(M = Si, Ge)$ groups are essentially identical. The basicity of the other alcohols decreases with increasing σ^* constants of the substituent attached to the OH group. The better correlation of relative basicities of the alcohols $\Delta\nu(OH)$ can be achieved

TABLE I

Relative Basicity and Relative Acidity of Alcohols ROH in CCl_4

R	$\Delta\nu(OH)$, phenol cm^{-1}	$\Delta\nu(OH)$, THF cm^{-1}
$(CH_3)_3SiCH_2$[a]	246	145
$(CH_3)_3C$	243	145[b]
$(CH_3)_3GeCH_2$[c]	243	150
$(CH_3)_3Si(CH_2)_2$[a]	240	149
$(CH_3)_3Ge(CH_2)_2$	240	150
$(CH_3)_2CH$	238	—
$C_2H_5(CH_3)CH$	236	—
$(CH_3)_3C(CH_2)_2$[c]	236	151
$(CH_3)_3CCH_2$	228	154
1-C_4H_9	230	—
1-C_3H_7	228	—
C_2H_5	227	154[b]
$C_6H_5(CH_2)_2$	227	—
CH_3	215	161[b]
$C_6H_5CH_2$	213	—
$CH_2{=}CHCH_2$	205	—
$Br(CH_2)_2$	199	—
$Cl(CH_2)_2$	189	164
Cl_2HCCH_2	155	208
Cl_3CCH_2	124	238

[a] Ref.[25]; [b] ref.[26]; [c] ref.[27].

by dividing the alcohols into alkanols and the hydroxy derivatives whose conformers can form intramolecular hydrogen bridge[11,39-41] (Fig. 1). Comparatively higher basicity of this series of alcohols (line 2) is then obviously due to this interaction. The lower basicity (deviation from the correlation line) of the alcohols ROH [R = = $(CH_3)_3C$-, $(CH_3)_3CCH_2$-, and presumably also $C_2H_5(CH_3)CH$-] could be explained by steric hindrance of the formation of the alcohol... phenol associate or by steric hindrance of the solvation of this associate.

TABLE II

Correlation of Relative Basicities and Relative Acidities of Alcohols RCH_2OH in CCl_4 with Constants of Polar Effect of Substituents R and RCH_2

Quantity correlated	Substituent constant	Number of data	Correlation coefficient	Denotation of correlation
Relative basicity	$\sigma^*(R)^a$	14	0·987	1
	$\sigma^*(RCH_2)^b$	16	0·977	2
	$\sigma_I(R)^{c,d}$	10	0·915	3
	$\sigma_I(R)^e$	4	0·882	4
	$\sigma_I(RCH_2)^f$	16	0·877	5
	$\sigma_I(R)^g$	6	0·456	6
Relative acidity	$\sigma^*(RCH_2)^{b,h}$	7	0·994	7
	$\sigma^*(R)^a$	7	0·965	8

^{a}Refs[28,29]; ^{b} Fig. 1; $\sigma^*(RCH_2)$ calculated as $\sigma_R^*/2\cdot8$; ^{c} ref.[30]; ^{d} ref.[31]; ^{e} ref.[32]; ^{f}ref.[33]; ^{g}ref.[34]; ^{h} Fig. 2; $Cl(CH_2)_2OH$ not included.

The degree of association of alcohols ROH with various proton acceptors and its influencing by substituent R were already studied with the use of IR spectroscopy. The integral intensity of the $v(OH)_{assoc.}$ band was successfully correlated with Taft σ^* constants of substituents R (ref.[42]). The possibility of correlating the free enthalpy of hydrogen bond formation with $\Delta v(OH)/v(OH)_{free}$ and with σ^* was confirmed also for association of the alcohols with acetonitrile[43]. The data just mentioned are in agreement with the order of relative acidities of the alcohols established in this work. The decrease of the acidity of alcohols ROH on going from $R = CH_3$ to the higher alkyls (Fig. 2) shows that the equilibrium reaction (2) is not controlled by the $-I$ effect of alkyl groups[60]. This effect would operate in ROH molecules, and particularly in their complexes with THF, in which case it would facilitate delocalization of the excess negative charge at the oxygen and stabilize the complex. The order of the relative acidities of alkanols in CCl_4 is consistent with the sequence of dissociation

constants of the alcohols in 2-propanol[44] and in water[45] $(K(CH_3OH) >$ $> K(C_2H_5OH))$. This indicates that intrinsic acidities of alcohols[46-51] in CCl_4 are also modified by solvent effect. In this case especially solvation of alcohols by THF must be assumed, because of high THF concentration used, but also solvation of alcohols by CCl_4 may be considered (see later). The dependence of the $\nu(OH)$ shifts of the alcohols induced by their interaction with THF on σ^* constants is shown in Table II (correlations 7 and 8); the relative acidities of the alcohols $(CH_3)_3Si(CH_2)_nOH$ $(n = 1,2)$ do not deviate from this correlation line. The effects of $(CH_3)_3MCH_2$- or $(CH_3)_3M(CH_2)_2$- groups $(M = Si, Ge)$ are again comparable (Table I). In this case, the relative acidity of the alcohols that form intramolecular hydrogen bond is not influenced by this interaction, since conformers without this hydrogen bond associate with proton acceptor more easily[43]. The deviation of 2-chloroethanol from the correlation line (Fig. 2) seems therefore surprising.

Solvation of alcohols by some aprotic solvents changes substantially their intrinsic equilibrium constants and can affect therefore also the characteristic quantities of their IR spectra (the intensity and wavenumber of the $\nu(OH)$ band) which could otherwise reflect the real molecular structure of these compounds. Solvation of alcohols by chlorinated solvents has been discussed in terms of interaction of the hydroxylic hydrogen with the negative atom of the solvent which is obviously controlled by the electron density of this atom[52]. The interpretation of the $\nu(OH)$ values of the alcohols RCH_2OH has most frequently been based on conformational heterogeneity and on the assumption that $\nu(OH)$ is determined above all by the type of

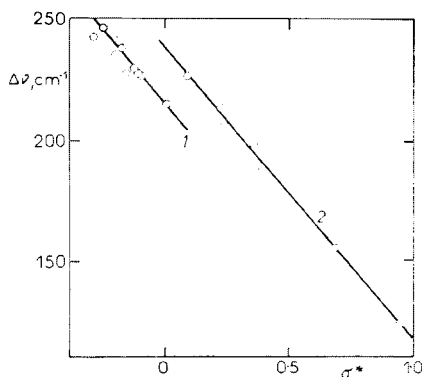FIG. 1

Dependence of $\Delta\nu$ (cm^{-1}) of ROH–Phenol System in CCl_4 on σ^*

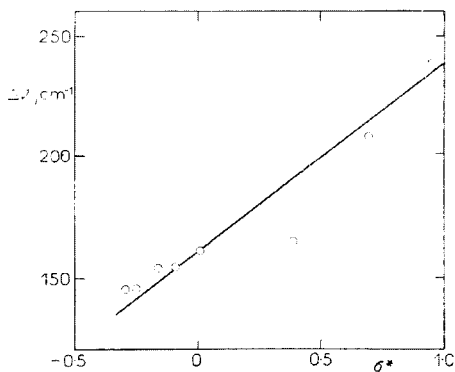The $\Delta\nu$'s taken from Table I.

Fig. 2

Dependence of $\Delta\nu$ (cm^{-1}) of ROH–THF System in CCl_4 on σ^*

The $\Delta\nu$'s taken from Table I.

conformer, *i.e.* by the precinct of the OH group $\left(e.g.^{53-55}\right)$. The explanation of the decrease of $v(OH)$ observed when going from primary to tertiary alcohols ROH by increasing total $-I$ effect of group R is not then quite correct, although the decrease of $v(OH)$ of the alcohols with increasing acidity was noticed[56]. The lower value of $v(OH)$ of the antiperiplanar conformer of ethanol relative to methanol in gas phase[57] and in CCl_4 $\left(e.g.^{53,58,59}\right)$ would indicate that the interaction of CCl_4 with ROH is not strong enough to cause that the alkyl group would influence the hydroxy group not by the $-I$ effect* but by electron-donating effect due to its polarizability. The electron acceptor ability of $(CH_3)_3MCH_2$- groups $(M = Si, Ge)$ was envoked to explain[62] also the lower $v(OH)$ of the alcohols $(CH_3)_3MCH_2OH$ in CCl_4 compared to $(CH_3)_3CCH_2OH$. Although relative basicity (see above) of these alcohols agrees with the electron-donating effect of $(CH_3)_3MCH_2$- groups, polarisability of $(CH_3)_3$ . . MCH_2- groups is not induced by solvation of molecules of $(CH_3)_3MCH_2OH$ $(M = Si, Ge)$ with tetrachloromethane.

Conformational population seems to complicate also comparison of the acidities of alcohols in CCl_4 evaluated from the intensities of $v(OH)$ bands. The accurate determination of this quantity requires comparison of solutions containing analogous rotamers in the same concentration. The argument that a certain significance can be attributed to intensities only in case that alcohols are represented predominantly by the same type of conformer may be however weakened by the fact that the process of gradual dissociation of the O—H bond during its vibration is controlled above all by polarisability of group R. The order of the intensities of $v(OH)$ of the alcohols ROH is not however consistent with this assumption: $CH_3OH > C_2H_5OH > (CH_3)_2$ . . $CHOH > (CH_3)_3COH$ (ref.[63,64]). The intensities of $v(OH)$ bands of primary alcohols show, however, the following trend: $CH_3OH < C_2H_5OH < n\text{-}C_4H_9OH$ (ref.[65]); $CH_3OH < (CH_3)_3CCH_2OH \simeq (CH_3)_3MCH_2OH$ $(M = Si, Ge)$ (ref.[62]). The latter data are not complicated by steric effects of neighbouring groups, which is the case with secondary and tertiary alcohols, since the alcohols $(CH_3)_3MCH_2OH$ $(M = C, Si, Ge)$ are represented mainly by one (*trans*) conformer. For that reason the above data could indicate that the $-I$ effect of alkyl groups is not significantly affected by solvation with CCl_4. The electron-accepting effect of $(CH_3)_3MCH_2$- groups is surprising in relation to the polarity of the Si—C bond and was ascribed to the back donation of electrons from the oxygen to the atom M, *i.e.* to the so-called α effect[62].

The better correlation of equilibrium data with σ^* than σ_I constants (Table II) confirms complex character of equilibrium data. These correlations indicate that the effects of solvation phenomena on studied equilibria in CCl_4 and on equilibrium reactions in water and related solvents result in the same order of relative equilibrium

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* The $-I$ effect of alkyl groups in molecules of ROH was pointed out in the work[60] which was however criticised[61].

constants, although the nature and extent of solvation in both systems is markedly different.

The determination of molecular effects in compounds $(CH_3)_3M(CH_2)_nOH$ from equilibrium data is then complicated. (The relative acidity is controlled above all by solvation phenomena, the relative basicity is controlled predominantly by polarisability of the groups attached to the OH group). Provided that solvation effects in the series $(CH_3)_3M(CH_2)_nOH$ with $n = 1$ and $n = 2$ are comparable, the order of relative acidities of the alcohols $(CH_3)_3MCH_2OH$, C > Ge > Si, can be explained by the lower ability of $(CH_3)_3MCH_2-$ groups $(M = Si, Ge)$ to stabilize complex IV. The interpretation of the order of relative basicity in the same series of the alcohols, C < Ge $\leqq$ Si, is influenced by steric effect of the $(CH_3)_3CCH_2-$ group. However, as molecular effects are more important in this case than solvation phenomena, from the correlation line 2 it follows that $(CH_3)_3MCH_2-$ groups $(M = Si, Ge)$ possess comparatively greater ability to stabilize complex III. This ability of $(CH_3)_3$ . . MCH_2- groups to stabilize both complexes indicates the absence of intramolecular interaction in these complexes which would otherwise decrease the electron-donating effect of $(CH_3)_3MCH_2-$ groups. The IR spectroscopic data (see above) speak however in favour of the occurrence of such interaction in the molecules of alcohols alone. The control of equilibrium data of the alcohols $(CH_3)_3MCH_2OH$ by the electron-donating effect of $(CH_3)_3MCH_2-$ groups in complexes III and IV should be therefore due to polarisability of these groups, *i.e.* by the extinction of intramolecular interaction resulting from the need of compensating the electron deficit on interacting oxygen (in complex III), or likely by electronic saturation of the atom M through σ bond (in complex IV).

Discussion of molecular effects in the alcohols $(CH_3)_3M(CH_2)_2OH$ is made difficult by small differences in equilibrium data and IR quantities for these alcohols $(M = Si, Ge)$ and $(CH_3)_3C(CH_2)_2OH$. The correlation of equilibrium data of the alcohols with σ^* constants (Table II, correlations 1 and 8) speaks for the electron-donating effect of $(CH_3)_3Si(CH_2)_2-$ (and also $(CH_3)_3Ge(CH_2)_2-$) group in complex III; intramolecular interaction of the O → M type is too weak or improbable.

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