

PROTON MAGNETIC RESONANCE STUDY OF ASSOCIATION OF TRIMETHYLSILYL SUBSTITUTED ALCOHOLS AND THEIR CARBON AND GERMANIUM ANALOGUES*

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PMR spectra of alcohols of the type $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OH}$ (where $\text{M} = \text{C}, \text{Si}, \text{Ge}$; $n = 1-4$) were studied in their concentration dependence in tetrachloromethane. The values of infinite dilution chemical shifts obtained by graphical extrapolation and of chemical shifts and association constants obtained by numerical calculations based on three association models were compared and the suitability of the models discussed.

Within the scope of our more extensive investigation of the chemistry of silyl- and germyl-substituted alcohols^{1,2} we have undertaken a study of their PMR spectra. For the sake of brevity the alcohols of the type $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OH}$, are denoted as $\text{M}\chi$ (where $\text{M} = \text{C}, \text{Si}, \text{Ge}$; $\chi = \alpha$ for $n = 1$, $\chi = \beta$ for $n = 2$, $\chi = \gamma$ for $n = 3$, $\chi = \delta$ for $n = 4$). Our aim was twofold: 1. to compare the alcohols among themselves and thus to attempt to shed some light on the bonding situation in their molecules, 2. to find the model which would describe their association. Since at the onset of our work tetrachloromethane was generally considered an inert solvent we had chosen this solvent as it offered also some advantages.

EXPERIMENTAL

Spectrometer. Spectra were measured on a Tesla BS 477 NMR spectrometer operating at 60 MHz. Positions of the spectral lines were determined by standard side band technique as averages of, at least, five measurements. Frequencies of the lines of OH, CH_2 and CH_3 positions were thus determined. The spectra were measured at $27 \pm 1^\circ\text{C}$.

Referencing. In an attempt to avoid tedious use of external reference, an inert internal reference was sought. Since nonbonded interaction influence the chemical shift³ of TMS, and since such interactions were reported⁴ to occur between silicon and oxygen⁴, it appeared necessary to test the inertness of tetramethylsilane towards alcohols. Our preliminary experiments showed that

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the methyl proton shifts, relative to internal TMS, in tetrachloromethane solution are concentration-dependent. For that reason cyclohexane was preferred as the internal reference though its line might at some alcohol concentration fall very close to the OH proton signal.

Solvent. Tetrachloromethane (Spectrograde, Lachema, Brno) was used as a solvent. Prior to its application it was dried by refluxing over P_2O_5 for 48 h and then distilled under dry nitrogen atmosphere. Water content was less than 0.009 mg $H_2O/1$ ml CCl_4 .

Alcohols. The alcohols were prepared in our laboratory. Their preparation and physical constants were reported elsewhere^{1,2}.

Solutions. About ten solutions of each alcohol were prepared by weighting. The concentrations of the solutions were kept in the 0.002–0.8 mole fraction range.

Calculations. All numerical calculations were performed on N.R.C. Elliot 4120, equipped with a plotter. Programs were written in Algol language.

RESULTS AND DISCUSSION

In the studied alcohols the shifts of OH protons are most sensitive to concentration changes; the more a C—H bond is remoted from the OH group, the less is the chemical shift of the CH proton dependent on concentration⁵. The experimental hydroxyl proton chemical shifts are given in Table I together with the infinite dilution values obtained by graphical extrapolation (Fig. 1). The last values can be compared with the those determined from the dependences published by Storek and Kriegsmann⁶ and Davis and coworkers⁷ for the "zero" members of our series. In our scale, the infinite dilution shifts are for tert-butanol –35 Hz (see⁷) or –45 Hz (see⁶) and for trimethylsilanol –24 Hz (see⁶).

Similarly determined quantities have been used for comparison of basicities of alcohols^{8–10}. As expected, the infinite dilution shifts in proton acceptor solvents (dimethyl sulfoxide) correlate with the basicities of some silanols⁹, but surprisingly enough the variation of these shifts in DMSO with the structure of alcohols is paral-

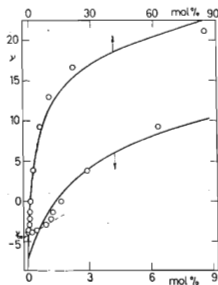


FIG. 1

Experimental Concentration Dependence of Hydroxyl Proton Chemical Shift in Si β Alcohol as Treated by the Lussan Model

The solid curve is the line of the best fit, the dashed line shows the method of graphical extrapolation.

TABLE I
Experimental Results^a

C α		Alcohol		C β		Alcohol		Ge β		Alcohol		Ge δ		Alcohol		Ge γ		Alcohol		Si β		Alcohol		
Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	
44.6	190.4	84.1	213.8	87.1	218.2	88.0	222.9	84.9	217.1	86.2	211.0													
22.9	165.5	47.0	185.3	28.4	170.2	28.4	187.0	51.7	195.1	22.6	166.0													
12.3	129.9	50.4	194.4	8.8	114.4	30.7	191.5	29.9	186.8	10.9	129.3													
6.0	105.6	28.2	167.8	4.2	65.4	15.6	158.7	18.1	165.2	6.4	92.4													
2.6	0.0	11.3	134.5	2.2	23.4	10.8	152.3	13.2	118.7	2.9	37.4													
2.0	-15.5	5.4	82.4	1.5	0.0	5.0	69.2	5.4	89.0															
1.3	-13.0	3.8	64.5			3.7	77.8	2.8	58.5															
1.1	-23.4	1.35	-7.8	0.8	-22.6	1.8	0.0	2.05	25.6															
		1.1	-23.2	0.62	-29.8	0.99	-13.9	1.04	-8.1															
0.82	-27.4	0.85	-36.2	0.51	-33.0	0.83	-29.8	0.96	-25.2	0.89	-29.5													
0.69	-27.6	0.7	-40.6	0.22	-33.0	0.76	-29.8	0.93	-36.0	0.44	-36.4													
(0)	(-27 \pm 5)	0.47	-43.5	0.22	-33.0	0.63	-33.5	0.65	-39.0	0.22	-39.1													
		0.37	-47.2	(0)	(-35 \pm 5)	0.57	-33.4	0.63	-36.0	(0)	(-42 \pm 5)													
		(0)	(-53 \pm 10)			(0)	(-43 \pm 10)	(0)	(-45 \pm 10)															

TABLE I
(Continued)

Si γ	Alcohol	Si δ	Alcohol	Ge α	Alcohol	C γ	Alcohol	C δ	Alcohol	Si α	Alcohol
Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift	Conc.	Chem. shift
80.2	220.4	87.8	212.6	86.7	188.0	86.6	225.4	88.9	224.9	88.4	253.6
30.0	189.8	27.2	183.1	44.3	160.9	29.6	186.6	26.6	184.6	32.9	108.8
8.4	130.1	6.9	106.8	20.8	128.4	10.9	142.7	21.6	179.3	9.0	81.3
4.5	90.0	4.2	89.0	12.9	98.7	3.9	46.5	10.2	145.1	4.4	22.6
2.3	10.6	1.94	29.5	4.7	17.3	2.1	39.0	4.4	78.9	2.1	25.6
(0)	^b	1.45	9.7	1.6	-38.2	1.0	-22.5	2.6	6.8	1.09	-29.6
		1.08	5.9	0.85	-33.5	(0)	^b	1.9	40.3	1.0	-39.4
		0.47	-36.0	0.52	-36.7			0.33	-38.9	0.77	-44.3
		0.24	-36.9	0.35	-36.3			(0)	(-45 ± 10)	0.56	-47.8
		(0)	(-40 ± 10)	(0)	(-36 ± 5)					0.28	-49.1
										(0)	(-50 ± 5)

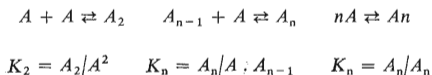
^aConcentration in tetrachloromethane in mole fraction $\times 100$. Chemical shifts in Hz relative to internal cyclohexane. Negative values indicate shifts to higher field. Values in parentheses were obtained by graphical extrapolation. ^bThese values could not be determined precisely enough.

leled (with a few exceptions) by the variation of their infinite dilution shifts in tetrachloromethane and thus $\nu_{\infty}(\text{DMSO}) - \nu_{\infty}(\text{CCl}_4)$ remains essentially constant¹⁰. Though it may be fortuitous the variations in the infinite dilution shifts determined here seem to support the ideas put forward by Allred, Rochow and Stone⁸ that in the silanol the ($p \rightarrow d$) π bonding Si—O leads to a decrease in OH proton shielding. In the α -derivatives this effect is not present due to the isolating effect of the CH_2 group and only the inductive effect is operating. The inductive effect of $(\text{CH}_3)_3\text{M}$ group on OH proton shielding is further diminished by additional intervening CH_2 group. There are practically no differences between β , γ , and δ derivatives. This conclusions should be taken with great reserve since such reasoning cannot explain the relative shift in $\text{C}\alpha$ and $\text{C}\beta$ alcohols and is based on very crude values and moreover, it neglects all other effects which are certainly also operating^{9,10} especially in the germanium series.

Quantitative characteristics which might allow more serious comparisons between alcohols to be made can be derived from the whole concentration dependences of OH proton chemical shifts. The characteristics and their values rely upon the association model and the method of calculation employed. Meaningful quantitative parameters (dilution shifts, equilibrium constants, *etc.*) are obtained only if their calculation is based on a correct model for the association equilibrium. For the correct model is usually taken that which gives of all the models suggested the closest fit of experimental data in a significant number of experiments.

Of the many association models possible, we have tested three which seemed appropriate to the association of our alcohols. All the three models¹¹⁻¹³ treat binary mixtures in the whole concentration range assuming an inert solvent. Activity coefficients of all species in solutions are taken to be equal to one at all concentrations. In interpreting NMR data the models assume only two magnetically different types of OH protons; one, with the chemical shift ν_n , is in the middle of the chain of associates and is engaged in H-bonding. The other OH protons are at the end of the chain and in monomeric species. They are not involved in H-bonds and have the shift ν_1 .

The differences between the models are conveniently described if the following symbols are introduced. The molecule of a monomer is denoted by A , the n -mer associate by A_n , and K_n 's are the association constants pertaining to the association equilibria. (Mole fraction units are used for concentrations throughout this paper).



Then: 1. The model according to Lussan¹¹ assumes that the n -mers A_n , have a linear structure and the association constants K_n do not depend on n ($K_n = K$). The observed shift (ν) relative to cyclohexane is given as

$$v = \{ \{ 2X_A^0 K + 1 - [4X_A^0 K(1 - X_A^0) + 1]^{1/2} \} (v_n - v_1) \} / \{ 2X_A^0 (K + 1) \} + v_1, \quad (1)$$

where X_A^0 is the analytical concentration of the alcohol in mole fraction.

2. LaPlanche¹² proposed a model in which the n -mers A_n are also linear and the association constants K_n for all n -mers larger than the dimer ($n > 2$) also do not depend on n but are different from the dimerisation constant K_2 ($K_2 \neq K_3 = K_4 = \dots = K_n = K$).

Then

$$\begin{aligned} v = & [1 + [A] \{ K_2 - 2K + [A] (K^2 - KK_2) \}] \cdot \\ & \cdot (v_1 - v_n) / [1 + [A] \{ 2K_2 - 2K + [A] (K^2 - KK_2) \}] + v_n, \\ & [A]^3 (K^2 - KK_2) (C + 1) + [A]^2 \{ K_2(2 + C) - K(2C + 2 + CK) \} + \\ & + [A] \{ 1 + C(1 + 2K) \} - C = 0; \quad \text{where } C = X_A^0 / (1 - X_A^0). \quad (2) \end{aligned}$$

3. In the model of Saunders and Hyne¹³ n -mers A_n are cyclic, the association constants for all the n -mers, except one, are equal and are much smaller than that for the one particular p -mer. ($K_n = K \ll K_p$). According to this model

$$\begin{aligned} v = & (p \cdot K_p [A]^{p-1} \cdot v_p + v_1) / (1 + [A]^{p-1} p K_p), \\ & [A]^p K_p \{ p(1 - X_A^0) + X_A^0 \} + [A] - X_A^0 = 0 \quad (3) \end{aligned}$$

Using the sets of Eqs (1)–(3) and the standard non-linear least squares method¹⁴ the chemical shifts v_1 , v_n and association constants K , K_2 , K_p were computed for each of the alcohols under study. The results of these calculations are summarised

TABLE II
Equilibrium Constants and Chemical Shifts Calculated According to LaPlanche Model^a

Alcohol	K	K_2	v_n	v_1	Δ^b
C α	36 \pm 4	0.3 \pm 0.3	193 \pm 10	- 25 \pm 5	50
C β	40 \pm 3	11 \pm 3	221 \pm 5	- 63 \pm 6	15
C δ	34 \pm 10	7 \pm 7	236 \pm 23	- 42 \pm 24	192
Si β	34 \pm 1	6 \pm 1	220 \pm 3	- 46 \pm 2	6
Si δ	44 \pm 5	14 \pm 5	225 \pm 8	- 50 \pm 9	28
Ge α	20 \pm 1	2 \pm 0.5	194 \pm 5	- 40 \pm 3	10
Ge β	30 \pm 2	8 \pm 1	227 \pm 5	- 42 \pm 3	9
Ge γ	36 \pm 4	6 \pm 4	231 \pm 10	- 46 \pm 11	62
Ge δ	51 \pm 20	37 \pm 38	238 \pm 16	- 103 \pm 50	86

^aThe errors indicated are RMS errors, units and signs are the same as in Table I. ^bSum of the squared deviations divided by the number of experimental points.

in Tables II and III. (Some alcohols had to be withdrawn from these tables because the experimental points either led to excessive errors in the association constants or the calculation diverged). The values given in Table III for the Saunders and Hyne model are those for "best" values of p which were found by trials – and – errors method. In cases of some alcohols, the results for several "best" values of p are presented because of insignificant differences in sums of squared deviations.

The results based on Eq. (1) are omitted from the Tables since the Lussan model gives the poorest agreement with the experiment. The failure of this model becomes clear from the Fig. 1. The theoretical curve, though roughly fitting the experimental one, does not reproduce its shape well enough, especially in low concentration region.

The theoretical curves corresponding to LaPlanche and Saunders and Hyne models reproduce the shape of the experimental dependence much better. Close inspection of Tables II and III reveals that our results do not permit to differentiate between the two models in question. Since this may be the consequence of the small number of measurements performed on each of our alcohols, data which would allow such a differentiation were sought in literature. The only data which were of value for our purposes were those on ethanol dissolved in tetrachloromethane^{7,15,16} and in cyclohexane¹⁷. The calculations described above were performed on these data, the

TABLE III
Equilibrium Constants and Chemical Shifts Calculated According to Saunders and Hyne Model^a

Alcohol	p^b	K_p	ν_n	ν_1	Δ^c
C β	3	$(4.5 \pm 0.6) \cdot 10^2$	223 ± 3	$- 54 \pm 3$	16
C γ	2	$(2.0 \pm 1.5) \cdot 10^1$	278 ± 25	$- 113 \pm 66$	129
	3	$(2.8 \pm 2.0) \cdot 10^2$	244 ± 16	$- 35 \pm 25$	133
C δ	3	$(3.4 \pm 1.7) \cdot 10^2$	244 ± 15	$- 40 \pm 18$	196
	4	$(1.1 \pm 0.7) \cdot 10^4$	229 ± 14	$- 33 \pm 18$	217
Si β	3	$(3.1 \pm 0.02) \cdot 10^2$	230 ± 2	$- 43 \pm 2$	4
Si δ	3	$(5.8 \pm 1.1) \cdot 10^2$	225 ± 6	$- 40 \pm 5$	31
	4	$(1.5 \pm 0.2) \cdot 10^3$	201 ± 3	$- 38 \pm 2$	7
Ge α	5	$(3.0 \pm 0.5) \cdot 10^4$	193 ± 3	$- 36 \pm 2$	8
Ge β	3	$(2.8 \pm 0.3) \cdot 10^2$	231 ± 3	$- 36 \pm 2$	9
	3	$(3.6 \pm 0.9) \cdot 10^2$	242 ± 8	$- 44 \pm 6$	65
Ge γ	4	$(1.0 \pm 0.3) \cdot 10^4$	228 ± 6	$- 33 \pm 5$	66
	2	$(2.3 \pm 0.7) \cdot 10^1$	261 ± 12	$- 114 \pm 23$	84
Ge δ	3	$(5.5 \pm 2.0) \cdot 10^2$	224 ± 8	$- 53 \pm 11$	104

^a The errors indicated are RMS errors, units and signs are the same as in Table I. ^b The "best" number of molecules in cyclic associates. ^c Sum of the squared deviations divided by the number of measurements.

TABLE IV
Ethanol Equilibrium Constants and Chemical Shifts Calculated from Literature Data^a

Author	Temp. °C	ν_0^f	La Planche model					Saunders and Hyne model				
			K	K_2	ν_n	ν_1	Δ^g	p^h	\bar{K}_p	ν_n	ν_1	Δ^g
Perotti ^{15b,d}	24	236	58 ± 4	9 ± 3	234 ± 4	-46 ± 7	38	3	(9.5 ± 1.6) · 10 ²	241 ± 3	-45 ± 5	44
Davis, Pitzer	22	237	38 ± 2	1 ± 5	228 ± 6	-29 ± 4	41	4	(4.5 ± 0.8) · 10 ⁴	231 ± 3	-33 ± 4	40
Rao ^{7b,e}								6	(1.2 ± 3.5) · 10 ⁶	230 ± 5	-26 ± 4	55
Becker, Liddel	27	236	55 ± 2	7 ± 2	236 ± 3	-44 ± 5	15	4	(4.0 ± 1.5) · 10 ⁸	227 ± 5	-24 ± 4	56
Chandler,	20	243	110 ± 6	9 ± 2	246 ± 2	-25 ± 9	10	4	(3.6 ± 0.5) · 10 ⁴	235 ± 2	-34 ± 3	17
Dinius ^{17c,e}								5	(3.2 ± 0.5) · 10 ⁵	248 ± 1	-26 ± 6	8.8
Chandler,	30	237	80 ± 2	7 ± 1	239 ± 1	-28 ± 4	5	4	(2.1 ± 0.3) · 10 ⁷	245 ± 1	-10 ± 4	8.4
Dinius ^{17c,e}								5	(1.1 ± 0.1) · 10 ⁵	241 ± 1	-24 ± 2	6.6
Chandler,	40	230	62 ± 2	5 ± 1	234 ± 2	-32 ± 3	6	4	(6.5 ± 0.8) · 10 ⁶	237 ± 1	-17 ± 2	7.6
Dinius ^{17c,e}								5	(5.4 ± 0.4) · 10 ⁴	236 ± 1	-27 ± 2	6.4
								5	(2.6 ± 0.3) · 10 ⁶	232 ± 1	-22 ± 2	9.6

^aThe errors indicated are RMS errors units and signs are the same as in Table I. ^bSolvent tetrachloromethane. ^cSolvent cyclohexane. ^d18 experimental points. ^e14 experimental points. ^fChemical shift in neat alcohol. ^gIn mole fraction units. ^hSum of the squared deviations divided by the number of measurements. ⁱThe "best" number of molecules in cyclic associates.

results are summarized in Table IV. Two conclusions emerge from a comparison of the results obtained for ethanol in tetrachloromethane solutions, namely, 1. the calculations yield essentially the same values of association constants and chemical shifts (ν_1 and ν_n) and the association numbers p if the same model is applied on the results obtained in different laboratories 2. again these results do not allow to differentiate between the two models. (Better agreement of experimental data¹⁶ in low concentration region with Saunders and Hyne than with LaPlanche model (Fig. 2) might be accidental). The measurements of ethanol in cyclohexane, though they also do not allow to differentiate between the two models, show for both models better fit. This may be caused either by "better experimental points" or by cyclohexane solutions meeting better the assumption on which the models are based. The latter possibility seems to be more probable since several authors recently pointed to association of tetrachloromethane with alcohols¹⁷⁻¹⁹. Such association could well cause the deviations we observed and it would also explain why $\nu_\infty(\text{DMSO}) - \nu_\infty(\text{CCl}_4)$ does not depend on the structure of alcohols¹⁰.

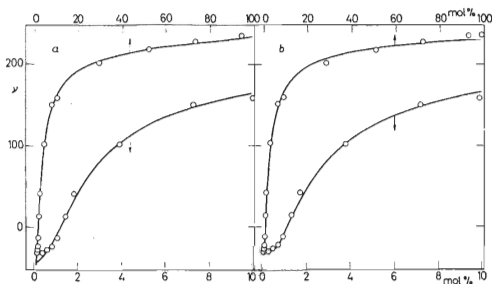


FIG. 2

Literature Concentration Dependence of Hydroxyl Proton Chemical Shift of Ethanol in Tetrachloromethane Treated by the LaPlanche (a) and Saunders and Hyne (b) Models

The failure of our calculations to distinguish the correct model is not surprising as it might seem at first sight. Both physically different models relate non-linearly the observed chemical shifts to four adjustable parameters. If the models could be distinguished on the basis of these measurements at all, considerably larger number of precise experimental points would be needed. This failure means also that it is impossible to determine the structure of n -mers, namely whether they are linear or cyclic.

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