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The Proton Nuclear Magnetic Resonance Spectra of Some Trialkoxysilanes

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The ^{1}H nuclear magnetic resonance spectra of some trialkoxysilanes ((RO)$_3$SiH; R = me, et, n-pr, i-pr, n-bu, i-bu, s-bu, t-bu) were examined, and chemical shifts and 29-silicon-proton spin-spin coupling constants were measured. The systematic trends found in these data for the silane proton in these and related compounds are thought to reflect changes in hybridisation of the silicon-hydrogen bond. A correlation is attempted between these data and the frequency of the silicon-hydrogen stretching vibration in the vibrational spectra.

Introduction

In connection with some work on the preparation of alkoxysilanes from silicon, the proton nuclear magnetic resonance spectra of some trialkoxysilanes were studied in order to measure the effect of substitution in the organic group on the chemical shift of the proton attached to silicon. This gave an opportunity to determine the coupling constants for the spin-spin interaction between the directly-bonded proton and the magnetically active isotope of silicon ($^{29}_{14}$Si) in the same compounds. The trends which were observed were compared with those noted in previous reports of the spectra of trialkylsilanes.[1-4] Later in this work an attempt was made to interpret these trends, and also to correlate the NMR data with the frequency of the silicon-hydrogen stretching vibrations in the vibrational spectra of the same compounds.

Previous reports of the spectrum of (meO)$_3$SiH gave both the chemical shifts and ^{29}Si–H spin-spin coupling constants (J(^{29}SiH). These papers were concerned principally with the effect of increasing substitution of methoxy- groups on the spectrum of monosilane.[5,6] The report on the spectrum of (etO)$_3$SiH gave only the chemical shift of the silane proton (τ(SiH))[2]. No other data on trialkoxysilanes were available. The spectra of many alkyl-, aryl, halo- and mixed- silanes have been reported[1-17] and some published work on stannane and methylstannanes[18] and some germanes[13,19-21] is also pertinent to this present work.

Results and Discussion

The chemical shifts determined in the present work are listed in Table I.

The assignment of resonances is made by comparison with the spectra of the parent alcohols and the spectra of other silanes, and is confirmed by integration.

It was observed in all cases that the protons on the α-carbon atoms in the organic groups of the trialkoxysilanes were shifted to lower field by 0.2-0.3 τ when compared with the spectra of the alcohols, while the shift for the other protons was about 0.05 τ downfield. This observation indicates that the protons in the organic groups of the silanes are deshielded to a greater extent than those in the alcohols, and this may be explained in terms of pπ–dπ bonding between the oxygen and silicon atoms more effectively removing electron density from the organic group,[22,23] *viz.*

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(1) D. E. Webster, *J. Chem. Soc.*, 5132, (1960).

(2) M. A. Khidekel, A. N. Egorochin, V. A. Ponomarenko, N. A. Zadorozhnyi, G. A. Razuvaev and A. D. Pctrov, *Izvest. Akad, Nauk S.S.S.R., Otdel. Khim. Nauk*, 1130, (1963).

(3) M. A. Jensen, *J. Organometal. Chem.*, *11*, 415, (1968).

(4) H. A. Brune, *Tetrahedron*, *24*, 79, (1968).

(5) H. J. Campbell-Ferguson, E. A. V. Ebsworth, A. G. Mac Diarmind, and T. Yoshioka, *J. Phys, Chem.*, *71*, 723, (1967).

(6) E. A. V. Ebsworth, *Pure Applied Chem.*, *13*, 189, (1966).

(7) E. Schnell and E. G. Rochow, *J. Inorg. Nucl. Chem.*, *6*, 303, (1958).

(8) H. Schmidbauer and H. Schindler, *J. Organometal. Chem.*, *2*, 466, (1964).

(9) O. Yamamoto and K. Hayamizu, *Bull. Chem. Soc. Japan*, *38*, 537, (1965).

(10) P. T. Narasimhan and M. T. Rogers, *J. Amer. Chem. Soc.*, *82*, 5983, (1960).

(11) K. M. Mackay, A. E. Watt and R. Watt, *J. Organometal. Chem.*, *12*, 49, (1968).

(12) E. A. V. Ebsworth and J.J. Turner, *J. Chem. Phys.*, *36*, 2628, (1962).

(13) A. N. Egorochkin, A. I. Burov, V. F. Mironov. T. K. Gar and N. S. Vyazankin, *Dokl. Akad. Nauk. S.S.S.R.*, *180*, 861, (1968).

(14) S. S. Danyluk, *J. Amer. Chem. Soc.*, *86*, 4504, (1964).

(15) S. S. Danyluk, *ibid.*, *87*, 2300, (1965).

(16) E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, *59*, 1518, (1963).

(17) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, *37*, 2198, (1962).

(18) N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, *85*, 1377, (1963).

(19) K. M. Mackay and R. Watt, *J. Organometal. Chem.*, *6*, 336, (1966).

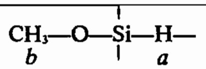
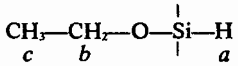
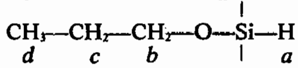
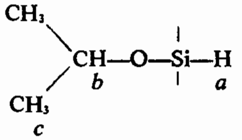
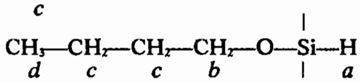
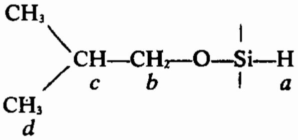
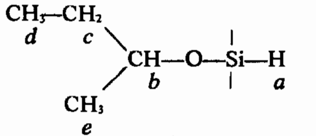
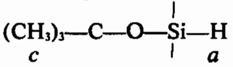
(20) L. Verdonck and G. P. van der Kelen, *Ber. Bunsenges. Physik. Chem.*, *69*, 478, (1965).

(21) L. Verdonck and G. P. van der Kelen, *Bull. Soc. Chim. Belges*, *76*, 258, (1967).

(22) V. Bazant, V. Chvalovsky and J. Rathousky, « *Organosilicon Compounds* », Czech. Acad. Sci. Press, Prague, 20, (1965).

(23) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, *1*, 112, (1955).

Table I. The nmr spectra of the compounds $(RO)_3SiH$ (R = me, et, n-pr, i-pr, n-bu, i-bu, s-bu, t-bu).

Compound		Chemical Shift (τ values) a	b	c	d	e
$(meO)_3SiH$	 $\underset{b}{CH_3}\text{—}O\text{—}Si\text{—}\underset{a}{H}\text{—}$	5.91(1)	6.47(1)	—	—	—
$(etO)_3SiH$	 $\underset{c}{CH_3}\text{—}\underset{b}{CH_2}\text{—}O\text{—}Si\text{—}\underset{a}{H}$	5.79(1)	6.18(4)	8.80(3)	—	—
$(n\text{—}prO)_3SiH$	 $\underset{d}{CH_3}\text{—}\underset{c}{CH_2}\text{—}\underset{b}{CH_2}\text{—}O\text{—}Si\text{—}\underset{a}{H}$	5.76(1)	6.27(3)	8.48(m)	9.08(m)	—
$(i\text{—}prO)_3SiH$		5.72(1)	5.78(7)	8.80(2)	—	—
$(n\text{—}buO)_3Si\ H$	 $\underset{d}{CH_3}\text{—}\underset{c}{CH_2}\text{—}\underset{c}{CH_2}\text{—}\underset{b}{CH_2}\text{—}O\text{—}Si\text{—}\underset{a}{H}$	5.76(1)	6.22(m)	8.50(m)	9.08(m)	—
$(i\text{—}buO)_3SiH$		5.75(1)	6.47(2)	8.27(m)	9.09(2)	—
$(s\text{—}buO)_3SiH$		5.64(1)	5.99(6)	8.60(m)	9.08(m)	8.80(2)
$(t\text{—}buO)_3SiH$	 $\underset{c}{(CH_3)_3}\text{—}C\text{—}O\text{—}Si\text{—}\underset{a}{H}$	5.49(1)	—	8.67(1)	—	—

((1) = singlet, (3) = triplet, (m) = multiplet, etc. Chemical shifts are quoted for center points of recognizable multiplets or for strongest resonance in distorted or complex multiplets).

Table II. Chemical shift, 29-silicon-proton spin-spin coupling constant and silicon-hydrogen stretching frequency data for some trialkyl- and trialkoxysilanes.

R	R_3SiH τ(SiH) [a, d]	J(^{29}SiH)	ν(SiH) [a, d]	$(RO)_3SiH$ [e] τ(SiH)	J(^{29}SiH)	ν(SiH) [f]
me	6.15	184.0 [b]	2120	5.91	291.6±0.3	2202
et	6.39	179.9 [c]	2105	5.79	288.2±0.2	2195
n-pr	6.32	—	2105	5.76	288.8±0.2	2195
i-pr	6.70	—	2092	5.72	284.8±0.2	2193
n-bu	6.34	180.4 [c]	2105	5.76	288.8±0.2	2195
i-bu	6.15	—	2114	5.75	289.7±0.3	2196
s-bu	—	—	—	5.64	284.7±0.3	2190
t-bu	—	—	—	5.49	282.6±0.2	2187

(τ(SiH) are in τ values; J(^{29}SiH) are in Hz; ν(SiH) in cm^{-1}; [a] = reference (1); [b] = reference (3); [c] = reference (4); [d] = 10% solutions in CCl_4; [e] = neat liquid samples; [f] = reference (37)).

It has been suggested previously that the values of the chemical shift of this proton on silicon (τ(SiH)), in the series R_3SiH (R = me, et, n-pr, i-pr, n-bu, i-bu), follow no obvious trend, and it was suggested further that the shielding may depend upon the number of protons on the β-carbon atom.[1] However, except for $(i\text{-}bu)_3SiH$, they appear to follow the order of inductive effect quite well. In contrast, this present work indicates a fairly steady decrease in τ(SiH), which is almost completely paralleled by J(^{29}SiH) for the silane proton, with increasing inductive effect from $(meO)_3SiH$ to $(t\text{—}buO)_3SiH$. These results are set out in Table II.

The pπ—dπ bonding between oxygen and silicon invoked to explain the downfield shift of the protons in the organic group of the trialkoxysilanes (when compared with the alcohols) is obviously not great enough to lead to increased shielding of the silane proton due to increased electron density on the silicon atom, as is shown by consideration of the spectra of the trialkylsilanes (see Table II). Although the factors which govern the chemical shift of the silane proton are still somewhat ill-defined, this low field shift in trialkoxysilanes can easily be explained by suggesting that the σ-withdrawal by the electronegative oxygen atom outweighs its π-donation. This reduction of electron density on the silicon atom, resulting in decreased shielding of the silane proton, also explains the increase in J(^{29}SiH) found when compared with the values for trialkylsilanes, because this coupling constant increases as the effective nuclear charge seen by the s-electron increases (see later).[24] But, it is thought that this pπ–dπ back bonding does contribute to the values found for τ(SiH) and J(^{29}SiH) and is important in explaining the trends found for these data in the trialkoxysilanes.

The Fermi contact contribution to the spin-spin coupling constant between two nuclei is directly proportional to the product of the electron densities of the two bonding orbitals at their respective nuclei. When hybridized orbitals are present, this contact contribution is proportional to the percentage s-character of the orbital used in forming the bond.[18,24-30] Assuming that the contact contribution is the dominant factor, then a decrease in J(^{29}SiH) might be expected to result from a decrease in the s-character of the silicon-hydrogen bond, which, within a given series of compounds like those presently under study, may also be reflected by a decrease in τ(SiH).

It has previously been observed that this multiple bonding between silicon and oxygen (and other elements) leads, for example, to an increase in the Si–O–Si angle in siloxanes to about 150°, and to approximately planar structures for $(H_3Si)_3N$ and $(me_3Si)_3N$ with Si–N–Si angles of about 115-120°.[6,22,23] In the trialkoxysilanes, the gradual decrease in J(^{29}SiH) and thus in s-character of the Si–H bond observed, is thought to result from a flattening of the SiO_3 grouping due to the pπ–dπ back bonding moving the oxygen atoms more closely into the plane containing the silicon atom. Thus, the O–Si–O angle would be increased to a value greater than that of a tetrahedron and so cause a rehybridization at the silicon atom, which may be expected to result in an increase in s-character of the Si–O bonds with a concomitant decrease in s-character of the Si–H bond (*i.e.* the orbitals used in bonding with the oxygen atoms are closer to sp^2 hybrids, while that used in the Si–H bond is a little closer to pure p).

Within this series of trialkoxysilanes, J(^{29}SiH) varies in the order meO > i–buO > etO ∼ n–prO = n–buO > i–prO ∼ s–buO > t–buO. This trend is closely paralleled by the order of τ(SiH), meO > etO > n–prO = n–buO > i–buO > i–prO > s–buO > t–buO (see Table II). These orders are almost exactly the reverse of those which might be predicted considering only the inductive effect, *i.e.* me < et < n–pr < i–bu < n–bu < i–pr < s–bu < t–bu.[31] This « reverse » trend may be explained by assuming that increasing inductive effect tends to strengthen the multiple silicon-oxygen bonding by increasing the electron density on the oxygen atoms. This would increase their π-donation and so result in a further decrease in the s-character of the SiH bond.

Steric interactions between the alkyl groups might also lead to a flattening of the SiO_3 grouping, with its concomitant effect on J(^{29}SiH). The order of steric effect in these alkyl groups is very similar to that for the inductive effect, and so these two factors would be complementary. However, it appears that the electronic effect is the more important as indicated by the position of $(i\text{–}buO)_3SiH$ in the order for J(^{29}SiH). The inductive factor of the i–buO group is similar to those of etO–, n–prO– and n–buO–, but it would be expected to produce greater steric effects than any of these. Table II shows that (J(^{29}SiH) for $(i\text{–}buO)_3SiH$ is similar in value to those for $(etO)_3SiH$, $(n\text{–}prO)_3SiH$ and $(n\text{–}buO)_3SiH$, thereby supporting this point of view. Other support comes from the trialkylsilanes. If it is assumed that τ(SiH) directly reflects J(^{29}SiH) (insufficient data for J(^{29}SiH) prompts this assumption), then if steric interactions are causing the decrease in s-character of the SiH bond, these effects should be greater here than in the trialkoxysilanes, and the shielding of the silane proton should decrease in going from me– to i–pr–. In fact, the reverse is observed, indicating that steric effects are not particularly important in this context.

Correlation between the SiH stretching frequency and the chemical shift of the silane proton. A correlation between ν(SiH) in the vibrational spectrum and τ(SiH) in the proton n.m.r spectrum has been attempted previously for many trisubstituted silanes, including $(etO)_3SiH$ and $(C_6H_5O)_3SiH$. The success of such correlations has been limited, and some deviations from the linear plot have been observed, particularly for those compounds containing unsaturated organic groups, alkoxy- or aryloxy- groups.[1,2]

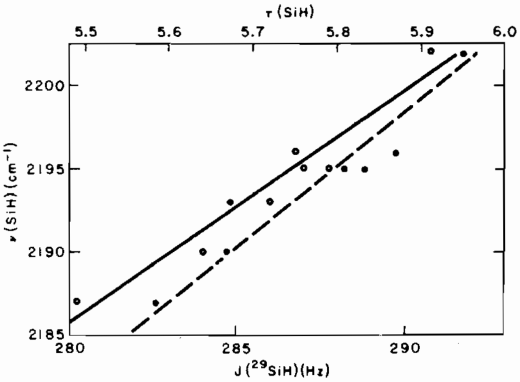


Figure 1. Plots of ν(SiH) *vs.* τ(SiH) (○ ——— ○) and ν(SiH) *vs.* J(^{29}SiH) (● — — — — ●) for the trialkoxysilanes.

In this present work, a fair linear correlation of these values has been found for the alkoxy- compounds over the rather abbreviated range of frequency and τ values used, and a similar fit is found for J(^{29}SiH) against ν(SiH) (see Table II and Figure 1). The most striking aspect of this ν(SiH) against τ(SiH) plot is the « reversed » slope found when compared with previous plots made for alkyl-, halo- and mixed

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(24) J. N. Shoolery, *J. Chem. Phys.*, 31, 1427, (1959).
(25) N. F. Ramsey, *Phys. Rev.*, *91*, 303, (1953).
(26) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, *30*, 6, (1959).
(27) N. Muller and D. E. Pritchard, *ibid.*, *31*, 768, (1959).
(28) N. Muller and D. E. Pritchard *ibid.*, *31*, 1471, (1959).
(29) N. Muller, *ibid.*, *36*, 359, (1962).
(30) M. Karplus, *J. Phys. Chem.*, *64*, 1793, (1960).
(31) R. W. Taft, jun., « *Steric Effects in Organic Chemistry* », Ed. Newman, John Wiley & Sons Inc., New York, Chap. 13, (1956).

silanes.[1,2] This difference is due to the fact that in the trialkoxysilanes, ν(SiH) and τ(SiH) increase together in the same order, while for the trialkylsilanes, for example, as ν(SiH) increases, so τ (SiH) decreases (see Table II).

Table III. Infrared and nmr data of the silane proton for some compounds R_3SiH

R	Electro-[a] negativity	ν(SiH)	τ(SiH)	J(^{29}SiH)
F	4.10	2315 [g]	5.49 [h]	381.7 [j]
Cl	2.83	2258 [e]	3.93 [h]	362.9 [j]
etO	3.50	2195 [k]	5.79	288.2
me$_2$N	3.07	2112 [f]	5.87 [d]	235 [d]
et	2.50	2105 [b]	6.39 [b]	179.9 [c]

(ν(SiH) in cm^{-1}; τ(SiH) in τ values; J(^{29}SiH) in Hz.; [a] = ref. (33), of atom attached to Si only, values for O and N would be lowered by R groups; [b] = ref. (1); [c] = ref. (4); [d] = ref. (5); [e] = ref. (32); [f] = ref. (34); [g] = ref. (35); [h] = ref. (36); [j] = ref. (12); [k] = ref. (37)).

It has been suggested that as electronegative groups on the silicon tend to increase ν(SiH), the electron density withdrawal that occurs causes a redistribution of electrons, resulting in an increase in s-character in the hydrogen directed orbital on silicon.[32] As this occurs, the bond becomes shorter and stronger, and so increases ν(SiH). This suggestion holds good over a wide range of compounds of the type R_3SiH (see Table III). The increase in s-character with increasing electronegativity is supported by similar increases in J(^{29}SiH). An increase in τ(SiH) in the same order, might possibly have been expected also, but Table III shows that, generally, as ν(SiH) increases, τ(SiH) decreases. This indicates that the shielding of the silane proton is affected, as expected, by factors other than changs in s-character, especially when great changes in the electronegativity of substituents occur. It would appear that replacing the weakly donating ethyl group by electron-withdrawing groups results in deshielding and a subsequent downfield shift for τ(SiH), even though the s-character of the SiH bond is increased. The greatest deshielding observed in Table III, for the chloro- compound, might be explained on the basis of the relatively poorer pπ–dπ back bonding which is thought to occur for chlorine when compared with fluorine, nitrogen and oxygen. This back bonding, in these latter compounds, would thus offset to some extent the electronegative deshielding effect. This sort of reasoning helps to explain the deviations found previously in ν(SiH) against τ(SiH) plots.

An alternative way of treating those trends in ν(SiH) and τ(SiH) is in terms of bond polarities. The relative electronegativities of hydrogen and silicon indicate that the polarisation of the bond should be $\overset{\delta+}{\underset{|}{\overset{|}{-\mathrm{Si}}}}\overset{\delta-}{-\mathrm{H}}$. Therefore, as electronegative groups withdraw electron density from the silicon, the silane proton should be deshielded and the bond polarity increased. This would give a stronger bond and thus an increase in ν(SiH), while showing a decrease in τ(SiH).

For trends within various series of compounds, factors other than these gross effects might also be important. For the trialkoxysilanes, where no great changes in electronegativity occur, it was shown in the previous section that as meO– was replaced by etO– and so on to t–buO–, so J(^{29}SiH) and τ(SiH) decreased due to a reduction of s-character in the SiH bond by a pπ–dπ « flattening » mechanism. Table II shows that as this occurs, so ν(SiH) also decreases. This is consistent with the gradual decrease in s-character in passing along this series. For trialkylsilanes, Table II shows that increasing inductive effect, which might be expected to decrease the polarity of the SiH bond and so decrease ν(SiH) and, at the same time, increase the shielding of τ(SiH), results in just this effect. Again, as was found in the trend of τ(SiH), (i–bu)$_3$SiH has an anomalous value for ν(SiH). However, both these values are consistent (see Table II), and indicate that if the inductive effect is the dominant factor here, then for this type of compound i-butyl has an inductive effect somewhere between methyl and ethyl. A similar result is indicated in the trialkoxysilanes (see Table II).

Experimental Section

(a) *Materials.* The compounds derived from primary alcohols were prepared by the copper-catalysed reactions of the alcohols with elementary silicon.[38] The other compounds were prepared by the reaction of trichlorosilane with the appropriate alcohol in benzene solution cooled in ice,[39,40] except for (t–buO)$_3$-SiH, when the preparation was carried out in the presence of pyridine.[41]

(b) *Spectra.* The spectra were recorded on a Varian Associates HA-100 Nuclear Magnetic Resonance Spectrometer operating at 100 MHz. In all cases, the data quoted herein were obtained on neat liquid samples. Spectra of solutions in carbon tetrachloride at various dilutions, *viz.* 5% and 50%, also were recorded when the variations in chemical shifts were found to be very small. In all measurements, tetramethylsilane was used as an internal standard.

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(32) A. L. Smith and N. C. Angeletti, *Spectrochim. Acta, 15*, 412, (1959).

(33) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, 5, 264, (1958).

(34) C. J. Attridge, *J. Organometal. Chem.*, *13*, 259, (1968).

(35) C. Newman, S. R. Polo and M. K. Wilson, *Spectrochim. Acta, 15*, 793, (1959).

(36) E. A. V. Ebsworth and J. J. Turner, *J. Phys, Chem.*, 67, 805, (1963).

(37) W. E. Newton and E. G. Rochow, publication in preparation.

(38) W. E. Newton and E. G. Rochow, publication in preparation.

(39) M. E. Havill, I. Joffe and H. W. Post, *J. Org. Chem.*, *13*, 280, (1948).

(40) I. Joffe and H. W. Post, *J. Org. Chem.*, *14*, 421, (1949).

(41) N. S. Nametkin, A. V. Topchiev and T. I. Chevnysheva, *Issled. v Obl. Kremnijorgan. Soedin., Sintez i Fiz-Khim. Svoistva, Akad. Nauk S.S.S.R., Inst. Neftekhim. Sinteza, Sb. Statei*, 5, (1962).