Studies of Silicon-29 Chemical Shifts in Methylsilyl Carboxylates by Heteronuclear Magnetic Double Resonance

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The ^{1}H and ^{29}Si chemical shifts in Me$_n$Si(O$_2$CR)$_{4-n}$ (n = 1—4) correlate linearly with the electron-withdrawing ability of the carboxylate group as measured by the pK_a of the acid RCO$_2$H. The relationships indicate that the ^{1}H shielding depends upon the effective charge on silicon whereas the ^{29}Si shielding varies with the electron imbalance in the Si–O bonds. It is not necessary to invoke *pπ–dπ* bonding to account for the results, and it is probable that silicon chemical shifts cover a wider overall range than do carbon shieldings.

CARBON-13 n.m.r. spectroscopy is now a widely used structural tool, and many empirical correlations between ^{13}C chemical shifts and structural features have been developed.[1] Some progress has also been made towards the theoretical understanding of carbon shielding,[2] but the position for other Group IV elements is much less satisfactory.[3] For silicon little systematic work has been done, and in published studies of ^{29}Si chemical shifts the compounds selected have been very diverse.[4–6] From the literature it appears that ^{29}Si chemical shifts extend over a much narrower range than do ^{13}C ones, and this has been attributed to *pπ–dπ* bonding in the silicon compounds.[4] However, silicon compounds analogous to those carbon ones which give the most extreme shifts have not been examined, and this may account for the narrower spread of the silicon data.

In this paper we present proton and ^{29}Si chemical shift data for three series of methylsilyl carboxylates, Me$_n$Si(O$_2$CR)$_{4-n}$ in which the electron-withdrawing ability of the carboxylate groups can be gauged from the pK_a of the parent carboxylic acid RCO$_2$H. This has the advantage that other factors (such as electric fields and van der Waals' forces) which might affect the silicon shielding, remain relatively constant, since the point of variation within a particular series is three bonds removed from the silicon atom. A similar approach has been used successfully in studies of ^{13}C shielding in methyl carboxylate esters,[7] and of ^{199}Hg–H spin coupling in methylmercury carboxylates.[8]

In contrast to earlier workers we have used a ^{1}H-{^{29}Si} double-resonance technique to obtain the silicon chemical shifts, and this offers considerable advantages in precision and sensitivity over conventional single-resonance experiments. It also makes it possible to use an internal reference, thus obviating bulk susceptibility corrections, and the ^{29}Si resonant frequencies can be related to a standard *proton* resonance.[9]

EXPERIMENTAL

The methylsilyl carboxylates were prepared by reaction between the appropriate methylsilyl chloride and the carboxylic acid in the presence of base (pyridine or triethylamine), or from the methylsilyl halide and silver carboxylate.[10] A correct b.p. and the absence of spurious peaks in the proton spectrum were usually taken as adequate criteria of purity, but previously unprepared compounds were analysed and the data are given in Table 1.

Proton spectra were recorded in frequency sweep mode on a spectrometer operating at 60 MHz using *ca.* 30% samples in CCl$_4$ which also contained small amounts of CH$_2$Cl$_2$ and tetramethylsilane to provide locking and reference signals respectively. Power at the ^{29}Si resonant frequency (11·91 MHz) was supplied to an extra coil in the probe by a Schlumberger FS 30 frequency synthesizer *via* a tuned amplifier. The frequency synthesizer was also used to control the 60 MHz spectrometer oscillator and the time base of the frequency counter used to calibrate the spectra, and the overall frequency stability was better than ±0·1 Hz for an indefinite period.

RESULTS

In the four series of compounds Me$_n$Si(O$_2$CR)$_{4-n}$ (n = 1—4) the coupling constant $^{2}J(^{29}\text{Si}\cdots\text{H})$ is 9·5, 7·1, 6·9, and

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[4] P. C. Lauterbur, *Determination of Org. Structures by Phys. Methods*, 1962, **2**, 465.

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6·0 Hz respectively, so that ^{29}Si satellites of the main methyl resonance were always clearly visible in the proton spectrum. Observation of these and ^{1}H–{^{29}Si} tickling experiments then gave the positions of individual components of the ^{29}Si multiplets to $\pm$0·2 Hz in most cases.[11] Care was taken to identify the centre of the silicon resonance correctly as an error of $J(^{29}\mathrm{Si}\cdots\mathrm{H})$ is equivalent to an error in the silicon chemical shift of almost 1 p.p.m. at our measuring field strength. The precision with which it was possible to perform the ^{29}Si tickling experiments showed that coupling between ^{29}Si and protons or ^{19}F nuclei in the carboxylate groups is negligible except in the case of the formates. In these $^{3}J(^{29}\mathrm{Si}\cdots\mathrm{H})$ was found to be 8·6, 7·1, and 6·0 Hz for n = 1, 2, and 3 respectively, and these values were confirmed by direct observation of the ^{29}Si satellites of the formyl proton resonances.

TABLE 1

Analytical data for methylsilyl carboxylates

Compound	B.p. [°C(mmHg)]	Calc. (%) C	Calc. (%) H	Calc. (%) Si	Found (%) C	Found (%) H	Found (%) Si
$Me_3Si{\cdot}O_2CBu^t$	30(10)	55·2	10·3	16·1	55·0	10·2	16·0
$MeSi{\cdot}O_2C{\cdot}CH{:}CHMe$	52(15)	53·2	8·85	17·7	53·1	8·8	17·5
$Me_3Si{\cdot}O_2C{\cdot}CH_2Ph$	92(4)	62·9	7·2	13·3	63·6	7·6	13·6
$Me_3Si{\cdot}O_2C{\cdot}CHCl_2$	63(14)	29·9	5·0	13·9	30·1	5·0	13·9
$Me_3Si{\cdot}O_2C{\cdot}CCl_3$	60(7)	25·5	3·8	11·9	25·3	3·75	11·6
$Me_2Si(O_2CBu^t)_2$	74(3)	55·4	9·25	10·8	56·3	9·2	10·5
$Me_2Si(O_2CH)_2$	55(8)	32·4	5·4	18·9	36·0	5·8	19·1
$MeSi(O_2CBu^t)_3$	91(1)	55·5	8·65	8·1	55·3	8·65	8·05
$MeSi(O_2CH)_3$	110(17)	27·0	3·35	15·7	27·3	3·45	15·5
$MeSi(O_2C{\cdot}CCl_3)_3$	188(4)	15·8	0·55	5·3	15·9	0·6	5·25

TABLE 2

Chemical shifts in methylsilyl carboxylates $Me_nSi(O_2CR)_{4-n}$

			$Me_3Si{\cdot}O_2CR$			$Me_2Si(O_2CR)_2$			$MeSi(O_2CR)_3$		
No.	R in RCO_2	pK_a of RCO_2H	δ-H(Me)/ p.p.m.[a]	$\Xi(^{29}Si)$/ Hz [b]	δ-^{29}Si/ p.p.m.[c]	δ-H(Me)/ p.p.m.[a]	$\Xi(^{29}Si)$/ Hz [b]	δ-^{29}Si/ p.p.m.[c]	δ-H(Me)/ p.p.m.[a]	$\Xi(^{29}Si)$/ Hz [b]	δ-^{29}Si/ p.p.m.[c]
1	Bu^t	5·02	0·253	19,867,634·3	22·6	0·442	19,867,277·0	4·6	0·630	19,866,376	−40·8
2	Me	4·76	0·253	19,867,629·3	22·3	0·452	19,867,272·0	4·4	0·648	19,866,336·7	−42·7
3	CH=CHMe	4·71	0·272	19,867,628·5	22·3						
4	CH_2Ph	4·30	0·233	19,867,663·5	24·0						
5	Ph	4·20	0·433	19,867,654·8	23·6	0·718	19,867,332·0	7·4	1·048	19,866,420	−38·6
6	H	3·75	0·310	19,867,686·5	25·2	0·546	19,867,323·8	7·0	0·770	19,866,371	−41·0
7	CH_2Br	2·89	0·317	19,867,715·7	26·7						
8	CH_2Cl	2·86	0·318	19,867,714·0	26·6	0·563	19,867,348·2	8·2	0·799	19,866,368	−41·2
9	$CHCl_2$	1·23	0·363	19,867,784·7	30·2	0·655	19,867,417·0	11·6	0·952	19,866,415	−38·8
10	CCl_3	0·66	0·425	19,867,831·7	32·5	0·750	19,867,440·0	12·8	1·088	19,866,438	−37·7
11	CF_3	0·22	0·400	19,867,844·7	33·2	0·727	19,867,464·3	14·0	1·037	19,866,420·8	−38·5
12	Et	4·87							0·640	19,866,346	−42·3
13	CH_2F	2·58							0·810	19,866,373	−40·9
14	$\begin{Bmatrix}CF_3\\CH_3\end{Bmatrix}$ [d]	2·49 [f]				0·590	19,867,379·5	9·8			
15	$\begin{Bmatrix}(H)_2\\Me\end{Bmatrix}$ [d]	4·09 [g]							0·727	19,866,383	−40·4
16	$\begin{Bmatrix}H\\(Me)_2\end{Bmatrix}$ [d]	4·42 [g]							0·689	19,866,365	−41·3

[a] To low-field of tetramethylsilane. [b] Resonant frequency in a polarizing field which gives a tetramethylsilane proton resonance at exactly 100 MHz. [c] To low field of $^{29}SiMe_4$. [d] Mixed species. [e] Taken from ref. 15. [f] Mean. [g] Weighted mean.

Some of the samples contained small amounts of hexamethyldisiloxane or related compounds produced by adventitious hydrolysis of the carboxylates. It was found that the presence of these, and of the acid produced simultaneously, had a negligible effect upon the silicon chemical shifts.

Similarly, the addition of small amounts (which were however greatly in excess of those actually present) of the base (pyridine or triethylamine) used in the preparation affected the silicon shielding by less than 0·3 p.p.m. In most of the compounds the silicon shielding was also found to be essentially independent of concentration in inert solvents, but for $Me_3Si{\cdot}O_2CCH_2Cl$ it was found that an addition of CH_2Cl_2 decreased the silicon shielding by 0·5 p.p.m. This effect was not investigated further. The temperature dependence of the chemical shifts was not studied, but analogy with carbon-13 shielding suggests that it should be slight. Recent double resonance studies of solvent effects upon ^{29}Si shielding in tetramethylsilane have also shown that these are small.[12]

DISCUSSION

Until recently it has been generally accepted that the shielding of nuclei other than the proton is dominated by the paramagnetic term [13] given by equation (1),[14] where

$$\sigma_{para} = \frac{A}{\Delta E}\{\langle r^{-3}{}_{np}\rangle Q_{np} + \langle r^{-3}{}_{nd}\rangle Q_{nd}\} \qquad (1)$$

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[12] M. Bacon, G. E. Maciel, W. K. Musker, and R. Scholl, *J. Amer. Chem. Soc.*, 1971, **93**, 2537.

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[14] H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, 1962, **37**, 2198.

ΔE is a mean electronic excitation energy which can be regarded as roughly constant in series of related compounds, $\langle r^{-3}{}_{np}\rangle$ and $\langle r^{-3}{}_{nd}\rangle$ are the average inverse cubes of the p and d electron–nucleus distances, and Q_{np} and Q_{nd} depend upon the p and d electron imbalance in the valence orbitals of the atom in question. A is a constant. For silicon an increase in the electronegativity of ligand will increase Q_{3p} thus increasing σ_{para} and giving a shift to low field, whereas Q_{3d} will be important only if there is π bonding involving silicon. The attachment of heavier atoms to ^{13}C, ^{29}Si, and ^{119}Sn has been found to lead to high-field chemical shifts, and this has been generally attributed to the effects of higher polarizability of the attached atom and/or π bonding.[3] However, it has been claimed that the diamagnetic contribution to the shielding is much more important than previously recognised and when the effect of immediate neighbours is considered most apparently anomalous ^{13}C chemical shifts can be accounted for.[2] In our series of compounds the diamagnetic contribution should be roughly constant for a given value of n, and the variations in silicon shielding as R is changed should therefore depend upon the paramagnetic term and hence upon changes in Q_{3p} and Q_{3d}.

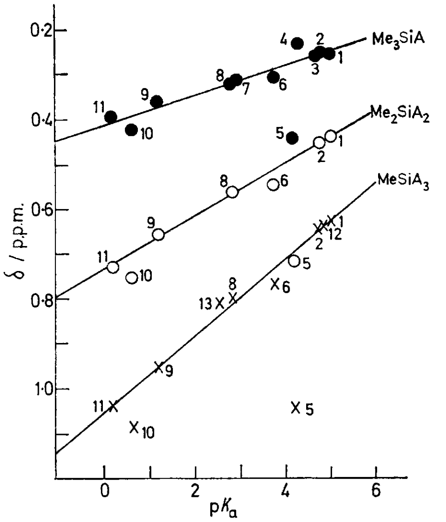

FIGURE 1 Proton chemical shifts (δ values in p.p.m.) of Si-methyl groups *vs.* pK_a of the parent acid RCO_2H (= AH) in methylsilyl carboxylates, Me_nSiA_{4-n}

The proton chemical shifts will depend upon the diamagnetic term and Figure 1 shows that there is a linear correlation between the methyl proton chemical shift and the pK_a of the parent acid[15] in each of the three series for $n = 1$—3. This shows that the electron density at silicon is indeed decreasing uniformly as the effective electronegativity of the carboxylate group increases.[16] Furthermore the three lines meet at a single point with $\delta = 0{\cdot}02 \pm 0{\cdot}01$ p.p.m. and p$K_a = 12{\cdot}3$, and their gradients are in the ratio $2{\cdot}9 : 2{\cdot}0 : 1{\cdot}1$, *i.e. ca.* $3:2:1$. These results show that the methyl proton chemical shift can be used to estimate the electron density on the silicon atom, and in particular that the relationship is not affected by altering the number of carboxylate groups attached to the silicon atom. The deviations observed for the benzoates can be ascribed to the diamagnetic anisotropy of the benzene rings. As was suggested[7] in ^{13}C studies of methyl benzoate the methyl groups will tend to lie near the plane of the aromatic rings and so will experience the observed deshielding.

The ^{29}Si chemical shifts in the series with $n = 3$ and 2 also show a good correlation with the electron density at silicon and there is a reasonable correlation for the series with $n = 1$. Domination of the shielding by the diamagnetic contribution would lead to three lines with gradients in the ratio $1:2:3$ for $n = 3$, 2, and 1 respectively as is found with the methyl proton chemical shifts, whereas the observed gradients are in the ratio $1 : 0{\cdot}88 : 0{\cdot}42$. These results are consistent with domination of the changes in silicon shielding in a particular series by variations in Q_{3p} which affect the paramagnetic term. An increase in the electronegativity of the carboxylate group will tend to increase Si–O bond electron imbalance by increasing the electron-withdrawing ability of the oxygen atom: but when $n = 1$ or 2 the electron density on silicon also will be reduced by the greater electronegativity of other carboxylate group(s) and so the net change in Q_{3p} will be correspondingly smaller.

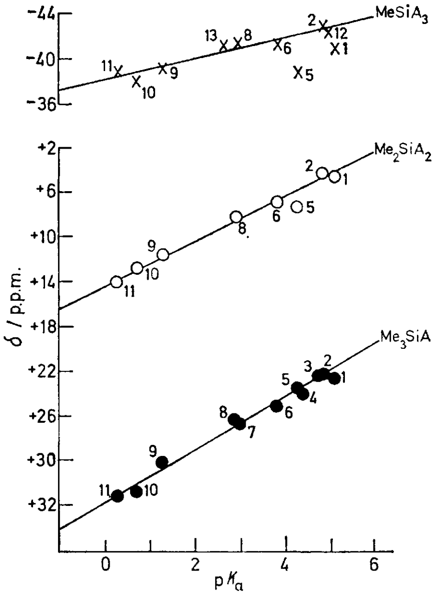

FIGURE 2 ^{29}Si Chemical shifts (in p.p.m. to low field of $^{29}SiMe_4$) *vs.* pK_a of the parent acid RCO_2H (= AH) in methylsilyl carboxylates, Me_nSiA_{4-n}

An alternative explanation of the smaller slopes found for δ (^{29}Si) *vs.* pK_a when n is small would involve $p\pi$–$d\pi$ bonding between oxygen and silicon. This would mitigate the electron-withdrawing effect when several

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[15] G. Kortüm, W. Vogel, and K. Andrussow, 'Dissociation Constants of Organic Acids in Aqueous Solution,' Butterworths, London, 1961.

[16] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon, Oxford, 1966, p. 666.

carboxylate groups are present and so the overall change in electron density at silicon would be smaller. However, the results for the methyl proton chemical shifts in the three series show that this is not so, and it therefore appears to be unnecessary to invoke π bonding to account for the ^{29}Si chemical shifts. If ^{29}Si and ^{13}C shieldings are dominated by the paramagnetic contribution, and π bonding is unimportant, as is almost certainly the case *within* a series for a particular value of n, equation (1) shows that in $^{13}CH_3O_2CR$ and $Me_3Si{\cdot}O_2CR$ the slopes of δ (^{13}C) and δ (^{29}Si) *vs.* the pK_a of RCO_2H should be proportional to $\langle r^{-3}{}_{2p\,(C)}\rangle$ and $\langle r^{-3}{}_{3p\,(Si)}\rangle$ respectively, provided that the mean excitation energies are comparable. In fact these two slopes are in the ratio 1 : 2·7 whereas the ratio of the mean inverse cubes of the valence p electron radii is *ca.* 1 : 1·3. That is, a factor of 2·1 remains unaccounted for, and the true range of ^{29}Si chemical shifts is probably greater than for ^{13}C. The limited evidence available [17] suggests that ΔE should not differ much in similar carbon and silicon compounds, even if there is some π bonding in the latter. Thus it appears that the electronic environment of silicon is more sensitive than that of carbon to perturbations brought about by changes in substituents. A similar conclusion was drawn [18] from a comparison of shieldings in selenium and phosphorus compounds, and the effect may be due to greater polarizability of the heavier atoms.

The increase in $^2J(^{29}Si \cdots H)$ as n decreases can be attributed either to an increase in the s character of the Si–C (methyl) bonds or to an increase in the effective nuclear charge of silicon as the electron-withdrawing ability of its substituents is increased.[19] In the former case the s character of the Si–O (carboxylate) bonds should *decrease* correspondingly, and so $^3J(^{29}Si \cdots H)$ should decrease as n is decreased in the series of formates. In the latter case both coupling constants should increase as n decreases, as is actually observed, so it appears that this mechanism dominates the changes in the coupling constants.

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[19] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.