STRUCTURAL CORRELATIONS BETWEEN SILYL RADICALS AND THEIR PARENT SILANES

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Summary

A good linear correlation exists between the ^{29}Si coupling constant of a silicon-centred radical and $J(^{29}Si-H)$ for the corresponding silane. Deviations from this line for chlorine and silicon substituents are interpreted in terms of delocalization in the radicals.

Results and discussion

The configuration of silicon-centred free radicals is of continuing interest; a recent theoretical study of the trimethylsilyl radical includes a good introduction to the pertinent literature [1]. ESR data and in particular ^{29}Si hyperfine coupling constants provide a direct measure of geometry at the radical centre. Such information is becoming increasingly available. We have recently shown that the ESR spectra of transient silyl radicals, obscured by the presence of persistent radicals, can be obtained by using intermittent illumination coupled with phase inversion of the spectrometer output [2]. Correlation analysis is a powerful method for locating the position of weak satellite spectra [3].

It is the purpose of this note to point out that a good linear relationship exists between the isotropic hyperfine coupling constant $a(Si)$ in a silicon-centred radical and $J(Si-H)$ from the NMR spectrum of the parent silane. Similar correlations have been reported for carbon [4,5] and phosphorus [6] centred radicals. $J(Si-H)$ has been previously associated with many measures of bonding and reactivity including Hammett and Taft substituent constants and the relative reactivities of Si-H bonds towards the CCl_3 radical [7].

A plot of $a(Si)$ against $J(Si-H)$ for twelve substituted silyl radicals is shown in the Fig. 1. The equation of a linear least mean squares fit to all the points is:

$$a(Si)/G = 1.576 \, J(Si-H)/Hz + 127.6$$

with a correlation coefficient of 0.983. This good correlation suggests that there is a linear relationship between the s character of the orbital containing the unpaired

electron in the radical and the *s* character of the silicon σ bonding orbital forming the Si–H bond in the parent silane.

However, inspection of a straight line drawn to include all the results shows that the points for $Si(SiMe_3)_3$ and $SiCl_3$ lie significantly below the line, indicating that for these radicals $a(Si)$ has a smaller absolute value than predicted. This suggests that electron delocalization is occurring onto the α-Si or Cl in these radicals. Accordingly, a least squares line was calculated for the seven compounds not possessing α-Si or Cl substituents, giving the slightly different straight line (shown in Fig. 1):

$$a(Si)/G = 1.625\,J(Si-H)/Hz + 123.9$$

with $r = 0.998$. The increase in the value of the correlation coefficient is not particularly significant in view of the smaller number of points and their grouping but the five radicals containing Si or Cl substituents all fall below the line, with the following deviations from the 'predicted' $a(Si)$ values: Si_2Me_5, 20.3; $Si(SiMe_3)_3$, 63; $SiMe_2Cl$, 15.4; $SiMeCl_2$, 28.8; $SiCl_3$, 49.9 G. These figures support the view that increasing substitution by silicon or chlorine lowers $a(Si)$ by an amount approximately proportional to the number of such substituents. This correlates with the removal of spin density from the radical centre, with a silicon substituent having a somewhat greater effect than chlorine.

Another point of interest which arises from this correlation is the apparently
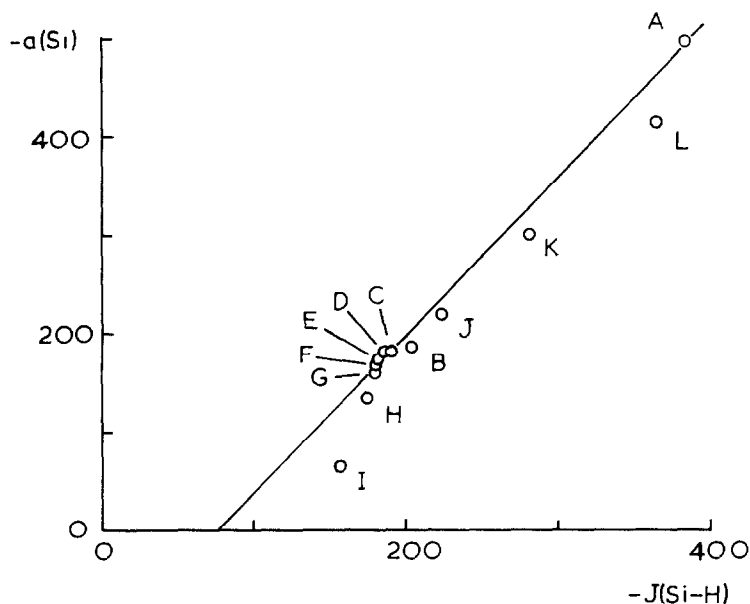

Fig. 1. (A) SiF_3, (B) SiH_3, (C) $SiMe_2H$, (D) $SiMe_3$, (E) $SiBu^tMe_2$, (F) $SiEt_3$, (G) $SiBu^t_3$, (H) $SiMe_2SiMe_3$, (I) $Si(SiMe_3)_3$, (J) $SiClMe_2$, (K) $SiMeCl_2$, (L) $SiCl_3$. ESR references: (A) M.V Merritt and R.W. Fessenden, J. Chem. Phys., 56 (1972) 2353; (B) G.S. Jackel and W. Gordy, Phys. Rev., 176 (1968) 443; (C), (D) P.J. Krusic and J.K. Kochi. J. Am. Chem. Soc., 91 (1969) 3938; (E) this work; (F) [3]; (G) [16]; (H), (I) J. Cooper, A. Hudson and R.A. Jackson, Mol. Phys., 23 (1972) 209; (J), (K) C Hesse, N. Leray and J. Roncin, J. Chem. Phys., 57 (1972) 749; (L) J. Roncin, Mol. Cryst., 3 (1967) 117. NMR references: (E) and (G) this work; other data from [7] and [11].

anomalous position of the triphenylsilyl radical. The ESR spectrum of Ph_3Si has not been observed in solution, probably because of its high reactivity towards aromatic substitution, although spectra have been reported for tris(3,5-di-t-butylphenyl)silyl [8] and trimesitylsilyl [9], Mes_3Si. A spectrum attributed to Ph_3Si has been reported in X-irradiated single crystals of Ph_3SiH [10]: the ^{29}Si hyperfine tensor yielded an isotropic coupling of 79.6 G. This value is much lower than the value of -198 G which we would predict from $J(Si-H)$ in triphenylsilane (-198 Hz) [11]. It also appears anomalous if we compare the central atom splittings in the series of silyl and germyl radicals MMe_3, MPh_3, and $MMes_3$. The reported values are 181, 79.6 [10], and 135 G [9] for $a(Si)$ and 84.7 [12], 84 [13], and 68.4 G [9] for $a(Ge)$. These results suggest that the structures of $GeMe_3$ and $GePh_3$ are very similar whereas there would appear to be significant structural differences between the corresponding silyl radicals. The ^{29}Si hyperfine tensor for $SiPh_3$ was actually obtained from the ESR spectrum of a radical-pair and a reexamination of this system would appear to be worthwhile.

Experimental

t-Butyldimethylsilane was prepared by reduction of the chlorosilane with $LiAlH_4$, b.p. 72°C (lit. [14] 73°C), $\delta(H)$ 0.00 (d, J 3.6 Hz, 6H), 0.89 (s, 9H), 3.61 (septet, J 3.6 Hz, 1H), $J(^{29}Si-H)$ 179.4 Hz. Tri-t-butylsilane [15,16] had $\delta(H)$ 1.12 (s,t-Bu), 3.33 (s,Si–H) ppm, $J(^{29}Si-H)$ 177.8 Hz.

t-Butyldimethylsilyl radicals were prepared from the silane by photolysis with di-t-butyl peroxide in the cavity of the ESR spectrometer. A 200 G scan range was used to obtain ESR spectra with the main spectrum on the right and left respectively. A higher gain was employed in the region away from the main spectrum, and an average of 2×8 min. scans was taken in each case. The proton hyperfine coupling constants are $a(Me)$ 6.4 G and $a(t-Bu)$ 0.6 G. ^{29}Si satellites were identified by the correlation technique MATCH [3] at positions 89.85 G downfield and 85.17 G upfield from the centre of the main spectrum, corresponding to $a(^{29}Si)$ 174.83 and 174.96 G respectively, average 174.9 G, using an exact solution of the Breit–Rabi equation [17].

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