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First observation of stable primary radical cations $^{t}Bu_3SiH^{+\cdot}$ formed by directed radiolysis of a pure compound: $^{t}Bu_3SiH$

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Abstract

Following γ-irradiation of neat $^{t}Bu_3SiH$ at 77 K, the ESR spectrum of the primary radical cation was observed; in contrast Et_3SiH yields only radicals arising from secondary processes.

1. Introduction

Radical cations are primary intermediates in the chemistry of neutral molecules in materials exposed to ionizing radiation. The simplest species of this kind are the radical cations of simple alkanes [1]. However, these are not observed spectroscopically following the direct irradiation of pure alkanes [2], although there was a recent report that ESR signals for some n-alkane radical cations could be observed, along with those from the counter-product of trapped electrons, when dilute solutions of a higher alkane were γ-irradiated in a matrix of a simpler alkane such as n-pentane [3]. More usually the radicals observed result from fragmentation or deprotonation of the primary radical cations and from recombination with ejected electrons, leading to dissociation of the excited neutral species.

We recently became interested in the behaviour of organosilanes on exposure to ionizing radiation, and we have now shown that, in contrast to simpler silanes such as Me_4Si, Me_3SiH, Me_2SiH_2 and $MeSiH_3$ (see ref. 4), and Et_3SiH (see later section), which give radicals by fragmentation and deprotonation and reflect a radiation chemistry similar to that of alkanes, $^{t}Bu_3SiH$ gives signals from the primary radical cations following direct radiolysis.

2. Results and discussion

2.1. $^{t}Bu_3SiH$

As shown in Fig. 1(a), after γ-irradiation of pure $^{t}Bu_3SiH$ at 77 K, clearly defined features are present in the ESR spectrum that can be assigned to the primary radical cations. This compound is therefore apparently resistant, at least at this low temperature, to the radiolytic reactions that are observed in all other cases studied to date, and this is a most unexpected result.

We confirmed that this species is $^{t}Bu_3SiH^{+\cdot}$ by the observation of a similar four-line pattern after γ-irradiation of a 1.0% solution of the silane in $CFCl_3$ at 77 K (Fig. 1(b)), since this procedure is well established to lead to primary substrate radical cations. The coupling constant is 43 G in the $CFCl_3$ matrix and 39 G in the self matrix and is similar to those observed [1] for $Me_4C^{+\cdot}$ (40 G) and $Me_3CH^{+\cdot}$ (48 G) radical cations. (These couplings also depend slightly on the type of matrix used.) This suggests a close structural relationship for all three radicals, and we propose that a SOMO of type I is present in $^{t}Bu_3SiH^{+\cdot}$, in which the *ca.* 40 G coupling arises from the three protons of a *single* ^{t}Bu group that are parallel to the C–Si bond, which is strongly electron-depleted. By analogy with the result [1] for the $Me_3CH^{+\cdot}$ radical cation, which shows a *ca.* 250 G splitting from the unique $C{-}H^{+\cdot}$

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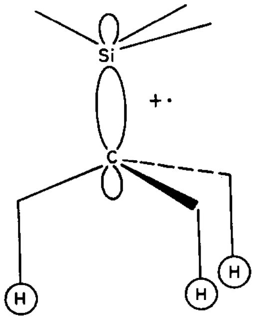
proton, we would expect an isotropic ^{29}Si coupling constant of *ca.* 150 G, and in the solid state a parallel ^{29}Si coupling of 180–190 G might be reasonable; however, the $-\mathrm{SiH^tBu_2}$ unit might be expected to "flatten" slightly on ionization and reduce this value. In any event, we observe no features in this expected region, and it may be simply that they are very broad, particularly given the rather wide spectrum from the central non-^{29}Si-containing species. There are features present which are almost certainly from ^{29}Si parallel components, but we prefer to assign them to $^t\mathrm{Bu_3Si^{\cdot}}$ radicals, given the good agreement with data [5] for other silyl radicals; the corresponding perpendicular features will be hidden under the signal from $^t\mathrm{Bu_3SiH^{+\cdot}}$ radical cations.



(I)

The rather sharp signal from $^t\mathrm{Bu_3Si^{\cdot}}$ radicals containing non-magnetic silicon nuclei is present in the centre of the spectrum. Its four-line structure points to the adoption of a specific conformation at 77 K of the type II, and is reminiscent of the behaviour of $\mathrm{R_2C{=}N^{+\cdot}{-}^tBu}$ radical cations, in which a particular conformation that transmits spin density to a single proton could be frozen-out at 77 K [6]. At 6 G, the coupling is very reasonable for a tert-butyl substituted silyl radical in view of previously reported results for the $^t\mathrm{BuSiMe_2^{\cdot}}$ radical in the liquid phase [7]. In that case, a coupling of 0.6 G was observed from all nine protons of the tert-butyl group, which was freely rotating about all C–C bonds on the ESR timescale: by averaging our 6 G coupling over 9 protons in a freely exchanging dynamic model, we obtain a very similar value of 0.66 G.

In the solid $\mathrm{CFCl_3}$ matrix we were able to observe dynamic changes on increasing the temperature, so that at 140 K the four-line (40 G) pattern collapsed into a broad band with a common splitting of *ca.* 13 G. As in the above examples, this must reflect a more rapid exchange of the nine methyl protons of the single tert-butyl group, so that their average value (roughly one third that for the "fixed" conformer) is observed. In the irradiated neat $^t\mathrm{Bu_3SiH}$ sample, irreversible chemical changes were observed on annealing, prior to any averaging of this kind. On recooling to 77 K, features were observed from tert-butyl radicals (Fig. 2), and so we propose that reaction (1) takes place at *ca.* 130 K, but that there is a finite activation energy associated with this.

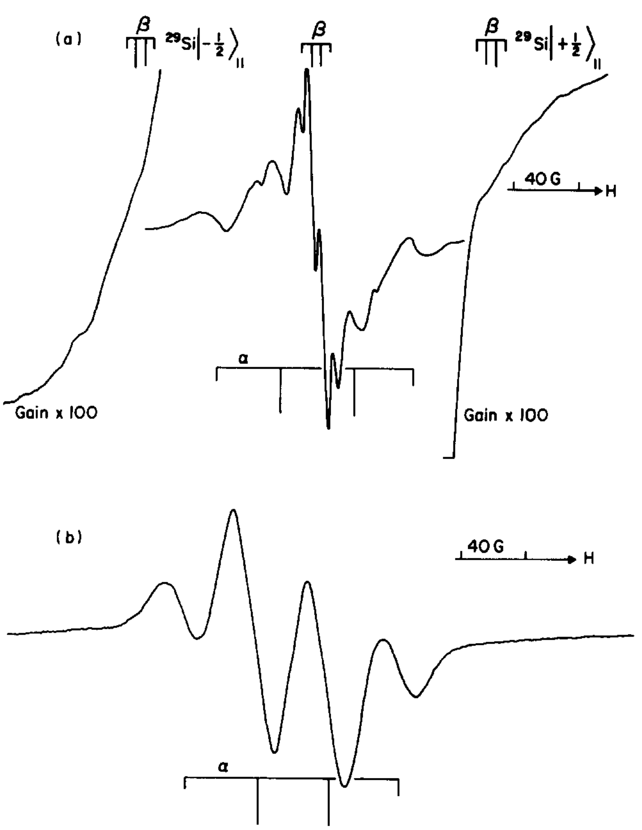
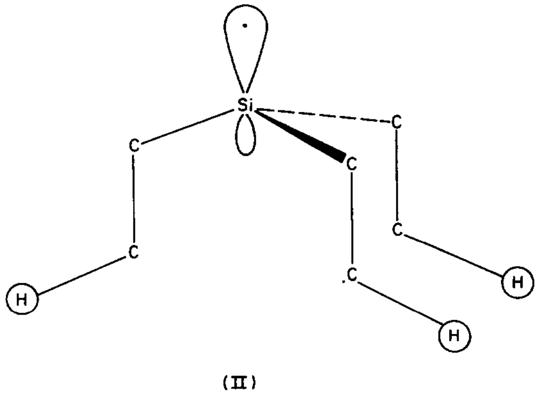


Fig. 1. (a) ESR spectrum recorded at 77 K from γ-irradiated $^t\mathrm{Bu_3SiH}$, showing features (α) from $^t\mathrm{Bu_3SiH^{+\cdot}}$ radical cations and (β) from $^t\mathrm{Bu_3Si^{\cdot}}$ radicals. Wing features recorded at increased gain are from the parallel ^{29}Si transitions in $^t\mathrm{Bu_3Si^{\cdot}}$ radicals. (b) Spectrum from authentically produced $^t\mathrm{Bu_3SiH^{+\cdot}}$ radical cations by γ-radiolysis of a dilute solution of $^t\mathrm{Bu_3SiH}$ in $\mathrm{CFCl_3}$ at 77 K.

$$^t\mathrm{Bu_3SiH^{+\cdot}} \longrightarrow {}^t\mathrm{Bu^{\cdot}} + {}^t\mathrm{Bu_2SiH^{+}} \qquad (1)$$



(II)

We attribute this to a barrier provided by the adoption of relatively more planar $Me_3C^{\cdot}$ and $^tBu_2SiH^+$ geometries in the dissociative transition state, due to the highly sterically hindered nature of the $^tBu_3SiH$ molecule. Nonetheless, a fragmentation of this kind should proceed more readily in the $^tBu_3SiH$ matrix, whose large molecules must provide less resistance to relaxation of the radical cation than the $CFCl_3$ medium which is able to stabilise the $^tBu_3SiH^{+\cdot}$ radical cation at least to its melting point (*ca.* 160 K).

Although it is possible that the $^tBu_3Si^{\cdot}$ radicals could arise from $^tBu_3SiH^{+\cdot}$ radical cations by deprotonation, this does not accord with the view of Iwasaki et al. [1], who proposed that such deprotonations occur from sites with high spin (charge) density, and our results show that the spin density at the Si–H hydrogen atom is negligible. If anything, deprotonation of $^tBu_3SiH^{+\cdot}$ radical cations should lead to H_2C–$C(Me_2)SiH^tBu_2$ radicals. It appears more likely that the $^tBu_3Si^{\cdot}$ radicals arise from an electron-gain centre since the signals of the $^tBu_3SiH^{+\cdot}$ and $^tBu_3Si^{\cdot}$ radicals are of comparable intensity, and we have detected no other radical that could be formed by capture of the electrons that must clearly be produced in this system by ionization. We suggest that reaction (2) occurs, since it is likely that dissociation of the $[^tBu_3SiH]^-$ radical anion could be driven by the hydride transfer (3) in the silane medium.

$$^tBu_3SiH + e^- \longrightarrow [^tBu_3SiH]^- \longrightarrow ^tBu_3Si^{\cdot} + H^- \qquad (2)$$

$$[^tBu_3SiH]^- + ^tBu_3SiH \longrightarrow ^tBu_3Si^{\cdot} + H_2 + ^tBu_3Si^- \qquad (3)$$

2.2. Formation of $^tBu_3SiOO\cdot$ radicals

In the low field region of the spectrum in Fig. 2 is an interesting "parallel" feature at $g = 2.083$; since this was present under these conditions only when oxygen was not excluded from the silane prior to radiolysis, we suggest that this is from the silylperoxyl radical formed by reaction (4)

$$^tBu_3Si^{\cdot} + O_2 \longrightarrow ^tBu_3Si\text{–}OO^{\cdot} \qquad (4)$$

It is significant that the g-feature is shifted much further from the free spin region than is the case for typical alkylperoxyl radicals [8], and we suggest the following explanation for this, by reference to Fig. 3. Firstly, we consider the situation for the superoxide radical anion. When the external magnetic field lies across the axis of the O–O bond (z), there is a strong orbital coupling between the $\pi^*(x, y)$ levels which are

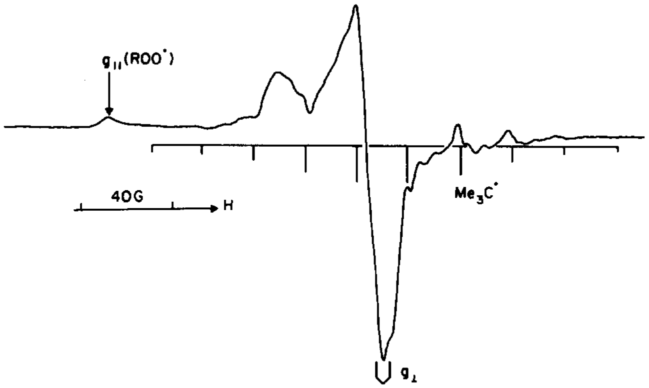


Fig. 2. ESR spectrum recorded at 77 K following annealing of the sample from (Fig. 1(a)) at 130 K, showing features from $Me_3C^{\cdot}$ radicals and from $ROO^{\cdot}$ radicals ($R = ^tBu_3Si$–; these latter were absent when degassed samples were used).

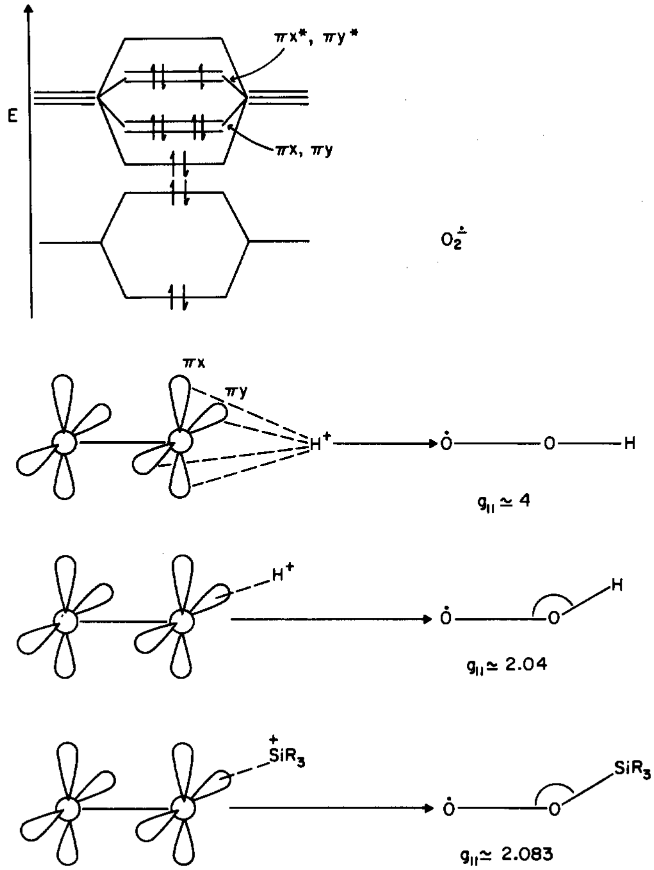


Fig. 3. Diagram depicting the (hypothetical) formation of the peroxyl radicals (shown) as a bonding perturbation of the orbitals in the $O_2^{-\cdot}$ radical anion, to explain the differing $g(z)$ shifts in these species (see text).

electronically degenerate: this leads, in turn, to a strong coupling of the electronic and spin angular momenta and consequently a large shift in $g(z)$ from free spin (the effects are far weaker when the field lies along the x or y axes, because the x, y degeneracy condition has no effect for these directions in first order). We can consider how a radical R(H)–O–O· might be formed by a hypothetical reaction between a proton (or other positively charged atomic centre) and the $O_2^{-\cdot}$ radical anion unit: if the bonding (with the σ–2p combination) is linear, as shown first, the electrostatic effect on the x, y levels in both the bonding and antibonding manifolds is the same. However, an angular bonding interaction, as shown next, will involve in addition the πx-levels, so that there is now a differential perturbation of the x, y levels in both bonding and antibonding manifolds, and the important $\pi^*(x, y)$ degeneracy is lifted, leading to a reduced $g(z)$ shift. In the silylperoxyl case, an additional O2p(π)-Si3d(π) interaction [9] with the πy level is expected, and will lead to a more linear structure: thus the perturbation is less and the angular momentum and the $g(z)$ shift greater than for an alkylperoxyl radical.

2.3. Et_3SiH

Figure 4 shows the ESR spectrum recorded from Et_3SiH, following γ-irradiation of the pure material at 77 K. In the central region is a pattern of six lines (α) with a common spacing of 24 G: this can be assigned to $CH_3CH_2^\cdot$ radicals, which are probably formed by radical cation-electron capture, leading to molecular excitation and bond homolysis (5).

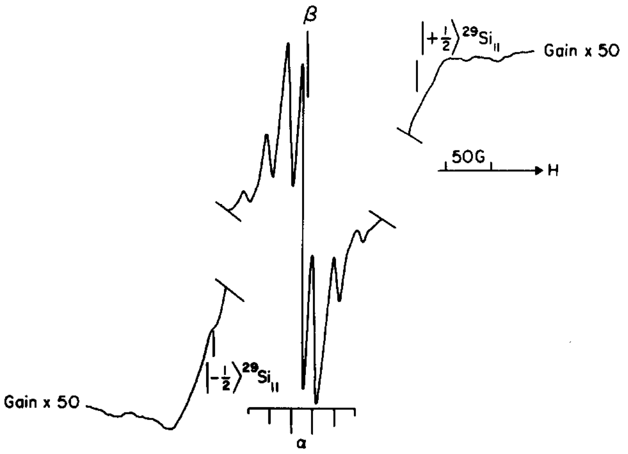


Fig. 4. ESR spectrum recorded at 77 K following γ-irradiation of Et_3SiH, showing features (α) from $CH_3CH_2^\cdot$ radicals and (β) from Et_3S. Wing features recorded at increased gain are from the parallel ^{29}Si (β) transitions.

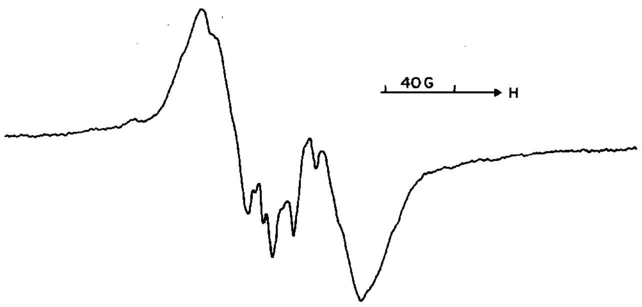


Fig. 5. ESR spectrum recorded at 77 K following γ-irradiation of Et_3SiH in a solid $CFCl_3$ matrix, showing features assigned to the primary radical cations.

$$Et_3SiH^{+\cdot} + e^- \longrightarrow [Et_3SiH]^* \longrightarrow Et^\cdot + Et_2SiH^\cdot \quad (5)$$

The alternative, of radical cation fragmentation (6), is not borne out by results obtained in Freon matrices, since the signal from the primary $Et_3SiH^{+\cdot}$ radical cation (Fig. 5) persisted up to the melting point of $CFCl_3$ (*ca.* 160 K), and at no time were ethyl radicals detected. However, as noted earlier for $^tBu_3SiH$, there may well be differences in the properties of Et_3SiH and $CFCl_3$ as matrices, so that reaction (6) cannot be definitely excluded.

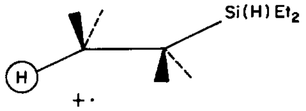
$$Et_3SiH^{+\cdot} \longrightarrow Et^\cdot + Et_2SiH^+ \quad (6)$$

The intense signal (β) is assigned to a silicon-centred radical, and from a mechanistic viewpoint it is reasonable to formulate this as $Et_2SiH^\cdot$, arising from eq. (5). However, there is no indication of α-H splitting, which would be expected as a doublet in the region of 16–17 G, in view of results for $Me_2SiH^\cdot$ [10] and $Ph_2SiH^\cdot$ [11]. Rather the feature appears to be a single peak, and so we assign it to the $Et_3SiH\cdot$ radical, assuming that the *ca.* 5 G coupling [12] to the β-protons is concealed within the linewidth. (The parallel ^{29}Si coupling, at 221 G is in good accord with that observed for other silyl radicals [5,11].) We propose that the source of this species may be the electron-gain centre, by analogy with reaction (2), although we cannot rule out Si–H bond homolysis in addition to the Si–C cleavage shown in eqn. (5).

2.4. $Et_3SiH^{+\cdot}$ radical cations in freon matrices

In order to obtain direct information about the structure and stability of authentic $Et_3SiH^{+\cdot}$ radical cations, we examined the ESR spectrum of Et_3SiH

following γ-radiolysis in a $CFCl_3$ matrix. As is clear from Fig. 5, this consists of a dominant doublet pattern, with some additional incompletely resolved structure. We suggest for this a structure (III) in which the SOMO is mainly confined to a single Et–Si unit giving rise to a relatively large (68 G) coupling to the terminal proton (shown). It is difficult to assess the spin density on the silicon atom, since we were unable to locate clear ^{29}Si features; however, comparison with results for the ethane radical cation [1], which in the Jahn/Teller distorted form, as observed at 4 K, shows couplings of *ca.* 150 G to two terminal protons, would suggest that this may be in the range of 46%, assuming that there is a similar *total* spin density at the terminal atoms in both cations. As mentioned earlier, this is a stable species under these conditions, and no secondary radicals were observed prior to the loss of the signal at *ca.* 160 K, which accompanies the softening of the $CFCl_3$ matrix: thus there is no support for reaction (6) as the origin of the ethyl radicals in the radiolysis of the pure silane.



(III)

3. Experimental details

Tri-tert-butylsilane (b.p. 92°C at 0.2 mmHg; lit. [13] 142–146°C at 100 mmHg) was prepared by reaction between trichlorosilane and tert-butyllithium to yield di-tert-butylchlorosilane, which was converted into di-tert-butylfluorosilane prior to a second treatment with tert-butyllithium [11]. Triethylsilane (b.p. 108°C; lit. [14] 108°C) was prepared by the reaction between trichlorosilane and ethyl magnesium bromide in ether solution. The pure silane or its dilute (0.1%) solution in $CFCl_3$, was frozen in a Suprasil ESR tube at 77 K and γ-irradiated to a dose of 1 Mrad, also at 77 K, from a ^{60}Co source. ESR spectra were recorded on a Varian E9 spectrometer, generally at 77 K, or at higher temperatures either (a) by decanting the liquid nitrogen coolant from the insert Dewar and allowing the sample to warm while continuously monitoring the ESR signal for any changes, and rapidly recooling to 77 K when such were observed, or (b) by using a Varian variable temperature apparatus.

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