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A study by electron spin resonance spectroscopy of the di-t-butylsilanone radical anion

Alwyn G. Davies and Anthony G. Neville
Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ (UK)

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Abstract

The ESR spectrum of the radical anion of di-t-butylsilanone $^{t}Bu_2Si{=}O^{\cdot -}$, can be observed when t-butoxyl radicals react with di-tert-butylsilanol under basic conditions. The magnitude of the hyperfine coupling to ^{29}Si shows that the radical anion is pyramidal at silicon.

Introduction

Great advances have been made in recent years in studies of multiple bonding to silicon. When the subject was reviewed in 1979 [1], all the evidence for silenes ($R_2Si{=}CR_2$), disilenes ($R_2Si{=}SiR_2$), and silanones ($R_2Si{=}O$) was indirect and inferential, being based on the identification of the products which were reasonably assumed to arise from reactions of these compounds, as unstable intermediates, with suitable substrates.

By 1985, when the subject was reviewed again [2], twelve silenes and seven disilenes had been isolated, and the crystal structures of eight of these compounds had been determined. The kinetic stability of all these compounds depended on the presence of four bulky substituents (*e.g.* mesityl, t-butyl, adamantyl, trialkylsilyl) at the ends of the double bonds, to inhibit oligomerisation sterically [3]. Further, since 1985 [4], examples of azasilenes ($R_2Si{=}NR$) and phosphasilenes ($R_2Si{=}PR$), where the double bond is protected by only three substituents, have also been obtained as stable compounds.

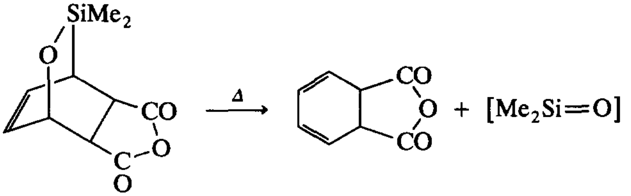
Silanones have still not been isolated, except in solid matrices, because only one end of the Si=O bond can be sterically protected by substituents, and this is not enough to prevent oligomerisation. The evidence for the formation of silanones thus depends on two types of experiment. In the first, silanones are generated as unstable intermediates in reactions such as those shown in eqs. 1 [5], 2 [6], and 3

Correspondence to: Professor A.G. Davies.

[7], and their formation is inferred from the products that they form by reaction with suitable substrates.

$$HMe_2SiOCH_2CMe_2CH{=}CH_2 \longrightarrow [Me_2Si{=}O] + Me_2C{=}CHMe \qquad (1)$$

$$(Me_2Si)_6 \xrightarrow{h\nu} [Me_2Si:] \xrightarrow[N_2O]{Me_2S{=}O} [Me_2Si{=}O] \qquad (2)$$


(3)

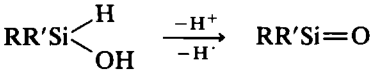
The second and more recent approach has been to trap or to generate (*e.g.* by reaction 4 [8]) the silanones in a solid argon matrix at *ca.* 12 K, and to characterise them by infrared spectroscopy [ν(Si=O) *ca.* 1200 cm^{-1}] [6–9].

$$Me_2SiH_2 + O_3 \longrightarrow Me_2Si{=}O \qquad (4)$$

We were interested in the possibility of learning more about these elusive silanones by studying the ESR spectra of their radical anions. Radical anions can be regarded as being the conjugate bases of neutral radicals, and we had shown that ketyl [10] and thioketyl [11] radical anions can be generated for ESR studies by the successive abstraction of a proton and a hydrogen atom from a primary or secondary alcohol or thiol (eq. 5, X = O or S).

$$R_2CH\text{-}XH \xrightarrow[-H^{\cdot}]{-H^+} R_2C{=}X^{\cdot-} \qquad (5)$$

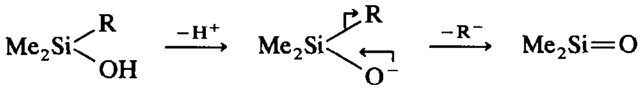
It therefore seemed likely that silanone radical anions might be formed by removal of a proton and a hydrogen atom, in either sequence, from a "primary" or "secondary" silanol.


(6)

$$RR'Si\begin{smallmatrix}H\\OH\end{smallmatrix} \xrightarrow[-H^{\cdot}]{-H^+} RR'Si{=}O \qquad (6)$$

This approach seemed to be particularly promising since silanols are more acidic than alcohols (*e.g.* Me_3SiOH compared with Me_3COH or Ph_3SiOH compared with Ph_3COH) [12,13] and alkoxyl radicals abstract hydrogen from an Si–H bond more readily than from a C–H bond [14].

Eaborn and Stańczyk [15] deduced from kinetic data that silanones themselves can be formed in an analogous process by loss of a proton and a carbanion R^- from the silanols RMe_2SiOH ($R = m\text{-}ClC_6H_4CH_2$ or $PhC{\equiv}C$) under basic conditions (eq. 7).


(7)

$$Me_2Si\begin{smallmatrix}R\\OH\end{smallmatrix} \xrightarrow{-H^+} Me_2Si\begin{smallmatrix}R\\O^-\end{smallmatrix} \xrightarrow{-R^-} Me_2Si{=}O \qquad (7)$$

Results

Diethylsilanol, di-isopropylsilanol, and diphenylsilanol are known species but undergo dehydration to the disiloxanes too readily to be suitable for our purpose.

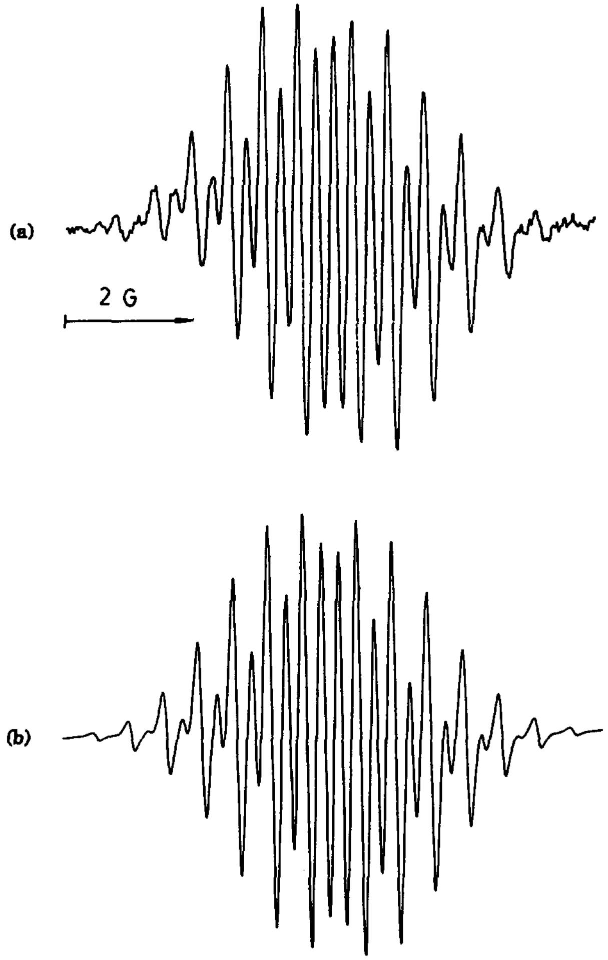


Fig. 1. (a) ESR spectrum of the di-t-butylhydroxysilyl radical **2** in t-butyl alcohol at 293 K. (b) Computer simulation.

Two t-butyl groups, however, provide enough steric hindrance to protect the silanol against dehydration, and di-t-butylsilanol (**1**) is a stable crystalline solid [16], and our initial studies were concentrated on this compound. Di-t-butylsilanediol can be distilled without decomposition at 210°C, and attempts to dehydrate it to di-t-butylsilanone gave instead 1,1,3,3-tetra-t-butyl-1,3-dihydroxydisiloxane [17,18].

When a solution of (**1**) and di-t-butyl peroxide in t-butyl alcohol was irradiated with UV light in the cavity of an ESR spectrometer at 293 K, the spectrum shown in Fig. 1a was obtained. This can be simulated as a doublet of 19-line multiplets (Fig. 1b) and at high gain, satellites due to ^{29}Si hyperfine coupling could be detected (^{29}Si, 4.70% natural abundance, I 1/2). We ascribe this spectrum to the di-t-butylhydroxysilyl radical **2**, a(H) 0.87 (OH), a(18H) 0.58 (^{t}Bu), a(^{29}Si) 186 G, ΔH_{pp} 0.1 G, g 2.0022. If the reaction was carried out in di-t-butyl peroxide as solvent, the same spectrum was obtained except that the coupling by the OH proton was absent.

$$\begin{tikzcd}
\underset{\mathbf{1}}{{}^{t}Bu_2Si(H)OH} \arrow[r, "{}^{t}BuO\cdot"] \arrow[d, "{}^{t}BuO^-"] & \underset{\mathbf{2}}{{}^{t}Bu_2\dot{Si}{-}OH} \arrow[d, "{}^{t}BuO^-"] \\
\underset{\mathbf{3}}{{}^{t}Bu_2Si(H)O^-} \arrow[r, "{}^{t}BuO\cdot"] & \underset{\mathbf{4}}{{}^{t}Bu_2Si{=}O^{\cdot -}}
\end{tikzcd}$$

Under the same conditions, di-t-butylethoxysilane gave rise to the spectrum of the radical ${}^{t}Bu_2\dot{Si}OEt$, with a(18H) 0.591 G, g 2.0024 at 263 K; a simulation using a(20H) 0.59 G was almost as satisfactory. The radicals $Me_2\dot{Si}OEt$ and ${}^{i}Pr_2\dot{Si}OMe$,

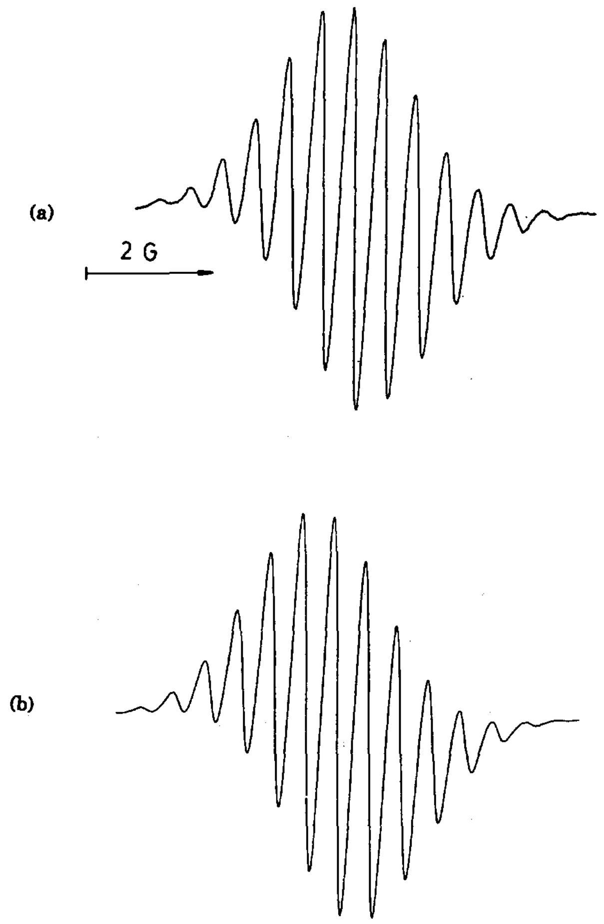


Fig. 2. (a) ESR spectrum of the di-t-butylsilanone radical anion **4** in t-butyl alcohol containing potassium t-butoxide. (b) Computer simulation.

prepared by a similar method showed a(6Hβ) 4.44, a(2H) 0.37, and a(2Hβ) 3.53, a(12H) 0.25, a(3H) 0.75, g 2.00228, and it is possible that in ^{t}Bu$_2\dot{\mathrm{S}}$iOEt the methylene protons have a hyperfine coupling of 0.59 G.

Photolysis of a solution of **1** in di-t-butyl peroxide and t-butyl alcohol containing potassium t-butoxide in excess with respect to the silanol gave the spectrum shown in Fig. 2, which can be simulated (Fig. 2b) as a 19-line multiplet, a(18H) 0.51, a(^{29}Si) 151 G, ΔH_{pp} 0.25 G, g 2.0025. The line-width was rather larger than that of the spectrum of **1**, but no change was observed when the concentration of potassium hydroxide was increased by a factor of five.

The change in the value of a(18H) and a(^{29}Si) and of g shows that the radical is not **1**, and from the loss of coupling by the OH proton, and the parallel with the behaviour of alcohols (eq. 5) we identify the new radical as being the di-t-butylsilanone radical anion **4**, which is probably formed principally *via* the silanolate ion **3**.

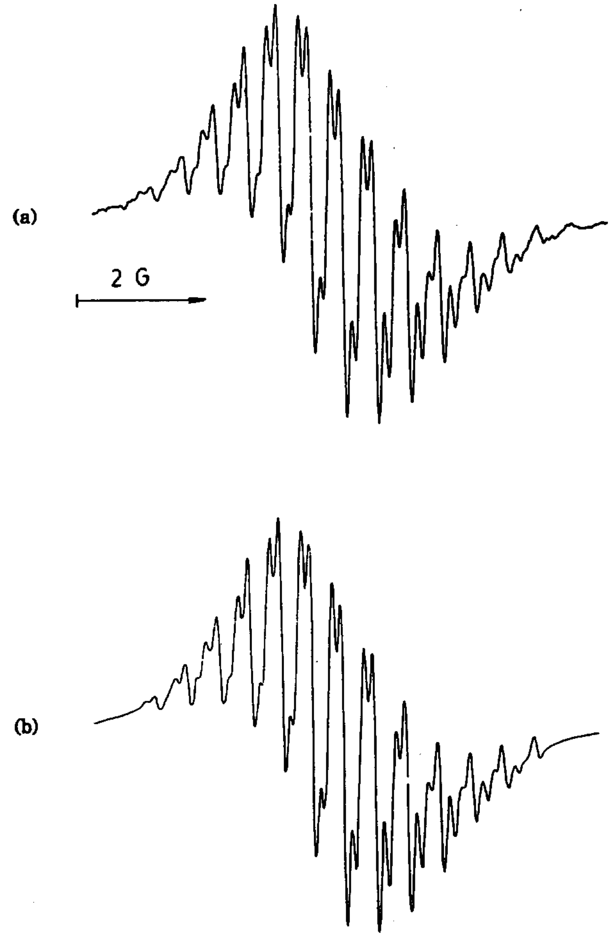


Fig. 3. (a) ESR spectrum of the di-t-butylsilanone radical anion **4** in t-butyl alcohol containing sodium t-butoxide, showing ^{23}Na hyperfine coupling. (b) Computer simulation.

When sodium t-butoxide was used instead of potassium t-butoxide, a third spectrum (Fig. 3a) was obtained. This can be simulated (Fig. 3b) as a 19-line multiplet split further by a 1:1:1:1 quartet coupling. We ascribe this spectrum to the silanone radical anion **4** with hyperfine coupling to the sodium counterion (^{23}Na, 100% natural abundance, *I* 3/2), *a*(18H) 0.50, *a*(^{23}Na) 0.28 G, *g* 2.0025, and this was confirmed by the fact that when the radical anion was generated in the presence of 18-crown-6, the quartet coupling was lost.

In an attempt to determine the degree of delocalisation of the unpaired electron onto oxygen, di-t-butylsilanol (**1**) was prepared with 10% ^{17}O enrichment (^{17}O *I* 5/2) but unfortunately no ^{17}O hyperfine coupling was apparent in the spectrum of either the radical **2** or the radical anion **4**. We must assume that either the hyperfine coupling is within the line-width, or that the satellites are broadened beyond detectability by the effect of the ^{17}O nuclear quadrupole.

Discussion

It is interesting to discuss these results on the hydroxysilyl radicals and silanone radical ions along the same lines used for the hydroxyalkyl radicals and alkanone radical anions [10,11].

The parent silanones and ketones probably have similar planar structures. X-ray crystallography shows that the azasilene, ^{t}Bu$_2$Si=NSi^{t}Bu$_3$ [19], is planar at silicon, and M.O. calculations suggest that the silanone is similarly planar with a bond order of 1.4 [2].

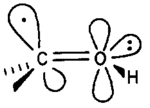
Simple alkyl radicals $R_nH_{3-n}C\cdot$ are near-planar; the unpaired electron is located in an orbital with essentially *2p* character, with a nodal plane at the carbon centre, and $a(^{13}C\alpha)$ is small; in the radical Me$_2$CH· it is 41.3 G [20]. Introduction of a ligand such as oxygen or fluorine at the carbon centre distorts it away from planarity, and $a(^{13}C\alpha)$ increases. Thus the radical Me$_2\dot{C}$OH shows $a(^{13}C\text{–}\alpha)$ 65.0 G [10] despite the fact that the unpaired electron now occupies a π^* orbital and is partially delocalised onto oxygen. The low hyperfine coupling constant (hfcc) of the OH proton (0.27 G), and its temperature dependence in related hydroxyalkyl radicals confirm that it lies close to the nodal plane of the π system. The radical can thus be represented by structure **5**.

This is accord with Pauling's principle that three-coordinate radicals should be pyramidal if the ligands are more electronegative than the central atom [21].

The alkanone radical anion is formed by removing this proton from the nodal plane, which leaves the electronic configuration basically unchanged as in **6**. The hfcc to the protons of the alkyl groups drops from 19.6 to 16.9 G, and $a(^{13}C\alpha)$ decreases from 65.0 to 52.2 G; the molecule is still clearly non-planar, but its structure cannot be compared quantitatively with that of its protic parent because the relative degree of delocalisation of the electron onto oxygen is unknown.

Whereas neutral alkyl radicals are essentially planar, simple silyl radicals $R_nH_{3-n}Si^{\cdot}$ are essentially pyramidal [22–25]. For example the radical Me$_3$Si$^{\cdot}$ shows $a(^{29}Si)$ 181.14 G, and as the isotropic coupling constant is *ca.* 800 G [26], the unpaired electron must occupy a $3sp^3$-type orbital. This is in accord with Pauling's principle and the relative electronegativities of silicon and carbon [21].

By analogy with the structures of both the hydroxyalkyl and the silyl radicals, the hydroxysilyl radicals would therefore be expected to have the pyramidal structure of 7, and this is confirmed by the ESR data for **2**. The value of $a^{29}Si$ of 186 G is larger than it is in the trimethylsilyl radical, despite the fact that the unpaired electron will be delocalised to some degree onto oxygen, and the small hyperfine coupling to the hydroxylic proton suggests that the OH bond lies close to a nodal plane. We conclude that the unpaired electron occupies an Si($3sp^3$)–O($2p$) π^* orbital, centred principally on silicon. The di-t-butylethoxysilyl radical has similar ESR characteristics and presumably has a similar structure.



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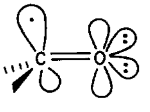

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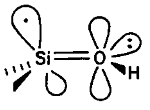

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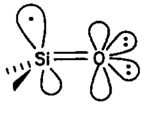

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Removal of the proton from **2** to give the silanone radical anion **4** appears to have a similar effect as it does in the deprotonation of the hydroxyalkyl radical **5** to give **6**. Hyperfine coupling to the protons of the alkyl groups is reduced slightly, and that to the central silicon atom is reduced by about 20% to 151 G. Again, however, it is not possible to interpret this quantitatively as the relative degree of delocalisation of the unpaired electron is not known. It is unfortunate that our attempts to determine this by ^{17}O labelling were not successful. Our conclusions regarding the stucture of the silanone radical anion are summarised in structure **8**.

Conclusion

The nuclear and electronic configurations of the hydroxyalkyl and hydroxysilyl radicals, and of the alkanone and silanone radical anions, thus appear to be closely related.

The principle which we have followed here for generating silanone radical anions can obviously be applied to the observation by ESR spectroscopy of the radical anions of other multiply bonded metallic compounds $R_2M=X$, where $M = Si$, Ge, Sn, or Pb, and $X = S$, NR, *etc.*

Experimental

Instrumentation

ESR spectra were recorded on a Varian E-109 spectrometer fitted with a standard temperature control unit, gaussmeter and field-frequency lock, an E.I.P. Autohet microwave counter model 331, and a Comark digital thermometer connected to a thermocouple in the cavity insert.

An Osram HBO-500 W/2 mercury discharge lamp in an Oriel Universal housing was focussed on the cavity, and provided with bronze gauze transmission filters (nominally 30, 10 or 3% transmission) and Pyrex and soda glass cut-off filters.

Di-t-butylhydroxysilane

A solution of sodium hydroxide (1.79 g, 44.8 mmol in *ca.* 45 cm^3 water) was added to di-t-butylchlorosilane (8.79 g, 49.2 mmol, Aldrich) in diethyl ether (*ca.* 25 cm^3) with phenolphthalein as an indicator, and the mixture was stirred at room temperature.

After 25 min the pink colour faded. After a further 45 min the organic layer was removed and washed with water (3 × 25 cm^3) and dried over magnesium sulphate. Removal of the ether and sublimation (20 mmHg, 60°C) gave di-t-butylhydroxysilane (6.92 g, 43.2 mmol, 88%), m.p. 64–66°C, identical with the material described by Barton and Tully [16].

Di-t-butylethoxysilane

Di-t-butylethoxysilane was synthesised by a procedure analogous to that used for di-t-butylmethoxysilane [16]. Dry ethanol (8.5 g, 0.18 mol) was added to a stirred solution of di-t-butylchlorosilane (8.86 g, 49.6 mmol) in pyridine (*ca.* 7 cm^3), which caused rapid evolution of heat and the precipitation of a white solid. The mixture was stirred overnight and the liquid phase was worked up with water, 2 *M* sulphuric acid, and saturated sodium bicarbonate solution.

After removal of low boiling residues by distillation, di-t-butylethoxysilane was obtained (7.50 g, 3.98 mmol, 81%). Anal. Found: C, 63.57; H, 12.65. $C_{10}H_{24}OSi$ calc.: C, 63.76; H, 12.84%. ^{1}H NMR (200 MHz; $CDCl_3$, TMS) δ 1.00 (18H, s, $C(CH_3)_3$), 1.20 (3H, t, OCH_2CH_3, J 6.98 Hz), 3.81 (2H, q, OCH_2CH_3, J 6.96 Hz), 4.00 (1H, s, SiH). ^{13}C NMR (200 MHz; $CDCl_3$, TMS) δ 18.33 (1C, q, OCH_2CH_3), 19.92 (2C, s, $C(CH_3)_3$), 27.26 (6C, q, $C(CH_3)_3$), 62.58 (1C, t, OCH_2CH_3). MS, m/z (relative intensity) 188 (M^+, 4.3), 103 (100), 131 (40.9), 89 (35.0), 73 (20.7), 75 (17.8).

Acknowledgment

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