E.s.r. Spectroscopic Observation of the Radical Anion of Di-t-butylsilanone, $Bu^t_2SiO^{\cdot -}$ A New Approach to the Study of Silanones

Alwyn G. Davies* and Anthony G. Neville

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

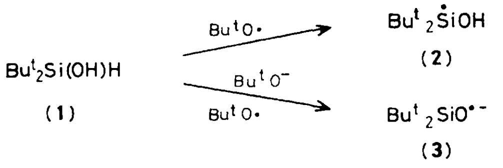
The e.s.r. spectrum of the radical anion of di-t-butylsilanone, $Bu^t_2SiO^{\cdot -}$, can be observed when di-t-butyl peroxide is photolysed in the presence of di-t-butylhydroxysilane, $Bu^t_2Si(OH)H$, under basic conditions.

Compounds containing Si=C and Si=Si groups (silenes and diselenes) have been isolated in recent years, but the Si=O compounds (silanones) have proved more elusive because they are more difficult to protect sterically against self-reaction to give oligosiloxanes.[1]

It is sometimes possible to exploit the sensitivity and selectivity of the e.s.r. technique, and the Coulombic protection against self-reaction which is intrinsic in a radical ion, to study a species $(S)^{\cdot -}$ when its parent (S) is unknown.[2]

We report here the application of this principle to the first observation of the radical anion of a silanone, $R_2SiO^{\cdot -}$.

Irradiation of a solution of di-t-butylsilanol[3] (**1**) in di-t-butyl peroxide gives a spectrum which can be simulated as a multiplet of 19 lines and which we ascribe to the di-t-butylhydroxysilyl radical (**2**). If the reaction is carried out in t-butyl alcohol as solvent, a further hyperfine coupling can be observed from the hydroxylic proton, together with ^{29}Si satellites.



When the t-butyl alcohol contains potassium t-butoxide, a spectrum (Figure 1) is again observed with intensities appropriate for a 19-line multiplet, but with different hyperfine

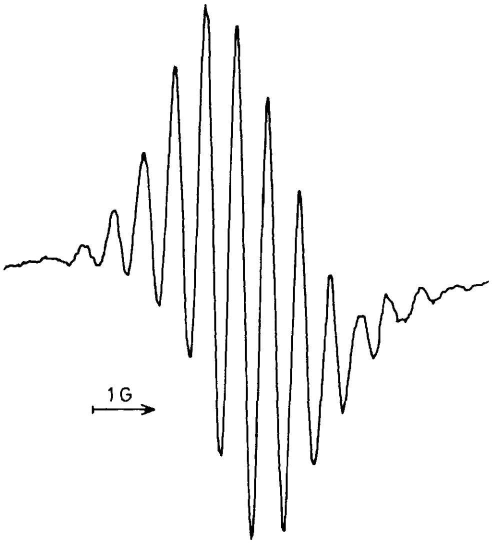


Figure 1. E.s.r. spectrum of $Bu^t_2SiO^{\cdot -}$ K^+ in Bu^tOH at 291 K.

Table 1. E.s.r. parameters of $\mathrm{Bu^{t}_{2}\dot{S}iOH}$ and of $\mathrm{Bu^{t}_{2}SiO^{\cdot -}}$.

		Hyperfine coupling constants/G[a]			
	Solvent	a(18H)	a(M)	$a(^{29}\mathrm{Si})$	g
$\mathrm{Bu^{t}_{2}\dot{S}iOH}$	$\mathrm{Bu^{t}OOBu^{t}}$	0.58	—		2.0020[d]
	$\mathrm{Bu^{t}OH}$	0.58	0.87[b]	186	2.0022[e]
$\mathrm{Bu^{t}_{2}SiO^{\cdot -}\ K^{+}}$	$\mathrm{Bu^{t}OH}$	0.51	—	150	2.0025[e]
$\mathrm{Bu^{t}_{2}SiO^{\cdot -}\ Na^{+}}$	$\mathrm{Bu^{t}OH}$	0.50	0.28[c]		2.0025[e]

[a] $G = 10^{-4}$ T. [b] M = H. [c] M = ^{23}Na. [d] At 233 K. [e] At 293 K.

coupling constants and g-value. These values are unchanged when the concentration of base is changed by a factor of three, and we ascribe this spectrum to the silanone radical anion (**3**) (see Figure 1).

If sodium t-butoxide is present instead of potassium t-butoxide, the spectrum shows a further quartet coupling from ^{23}Na, and this further coupling can be removed by adding 18-crown-6 to the solution.

Hyperfine coupling constants obtained by computer simulation, and g values, are given in Table 1.

The identification of these species is beyond reasonable doubt because of: (i) the way in which the radicals have been prepared,[4] (ii) the differences which are observed between the hyperfine coupling constants and the g values of the two species, and (iii) the observation of hyperfine coupling to the hydroxylic proton or to the Na^{+} counter-ion, which can be broken by standard methods.

The radicals $\mathrm{Me}_n\dot{\mathrm{S}}\mathrm{iH}_{3-n}$, n = 1—3, show values of $a(^{29}\mathrm{Si})$ of 181—183 G,[5] which imply that the unpaired electron is localised on silicon in an approximately sp^{3} orbital in a pyramidal radical.[6] The high value of $a(^{29}\mathrm{Si})$ of *ca.* 150 G which we find for the silanone radical anions shows that there is similar high spin density on silicon in a severely non-planar structure.

A similar approach can obviously be made to the study of the radical anions of other unstable compounds containing formal multiple bonds.

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References

1 References are given in G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419.

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3 Prepared in 88% yield by the hydrolysis of di-t-butylchlorosilane in ether with 1 M aqueous NaOH. The product was purified by sublimation and was identical with the hydroxysilane described by T. J. Barton and C. R. Tully, *J. Organomet. Chem.*, 1979, **172**, 11.

4 Hydroxyalkyl radicals, $\mathrm{R_2\dot{C}OH}$, and ketyl radical anions, $\mathrm{R_2CO^{\cdot -}}$, can be prepared in an analogous way from alcohols, $\mathrm{R_2C(OH)H}$: G. P. Laroff and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 1283.

5 Landolt-Börnstein, 'Numerical Data and Functional Relationships in Science and Technology,' 1979, II/9c2, 307—308.

6 H. Sakurai, in 'Free Radicals', ed. J. Kochi, Wiley, New York, 1973, vol. 2, pp. 761—767.