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Preliminary communication

AN ESR STUDY OF THE REACTIONS OF TRIALKYLSILOXYL AND TRIALKYLSILYL RADICALS WITH DIALKYL SULPHIDES

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Summary

Trimethylsiloxyl radicals add to dialkyl sulphides to produce sulphuranyl radicals, whilst triethylsilyl radicals bring about homolytic dealkylation of dialkyl sulphides.

The major reaction between t-butoxyl radicals and dialkyl sulphides of the type $(R_2CH)_2S$ (R = H, alkyl, or aryl) involves abstraction of an α-hydrogen to form the radicals $R_2\dot{C}SCHR_2$ (I), although attack at sulphur may be responsible for the ultimate formation of the sulphuranyl radicals $R_2CH\dot{S}(OBu\text{-}t)_2$ which have been detected by ESR spectroscopy [1]*.

$$\text{t-BuOOBu-t} \xrightarrow{h\nu} 2\ \text{t-BuO}^{\bullet} \qquad (1)$$

$$\text{t-BuO}^{\bullet} + (R_2CH)_2S \longrightarrow \text{t-BuOH} + \underset{\text{(I)}}{R_2\dot{C}SCHR_2} \qquad (2)$$

For example, when a cyclopropane solution containing di-t-butyl peroxide and dimethyl sulphide is irradiated with UV light whilst the sample is in the cavity of an ESR spectrometer the spectrum of the radical (I; R = H) is detected.

However, when the di-t-butyl peroxide was replaced by bis(trimethylsilyl) peroxide [3] overlapping spectra from I; R = H and from a radical showing a(6H) 7.7 G, g 2.0076 at 210 K were obtained. We assign the new signal to the sulphuranyl radical adduct II; R = H**.

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[*] The strained cyclic sulphide thietan undergoes attack at sulphur and ring-opening to yield the radical $t\text{-BuOSCH}_2CH_2CH_2^{\bullet}$ [2].

[**] A less likely alternative would be the sulphyranyl radical $(R_2CH)_2(ME_3SiO)S\dot{S}(CHR_2)_2$, produced by association of II with a second molecule of sulphide. Further work is in progress to distinguish between these two structures.

$$\mathrm{Me_3SiO^\bullet + (R_2CH)_2S} \begin{cases} \rightarrow \mathrm{R_2\dot{C}SCHR_2 + Me_3SiOH} & (3) \\ \rightarrow \underset{\text{(II)}}{\mathrm{(R_2CH)_2\dot{S}OSiMe_3}} & (4) \end{cases}$$

A similar competition between addition to sulphur and abstraction of hydrogen was observed for the reactions of trimethylsiloxyl radicals with a variety of dialkyl sulphides, and the results are summarised in Table 1. The ESR parameters for the sulphuranyl adducts of the type II are given in Table 2. It is not possible to deduce the detailed structure of II from the present isotropic ESR data. The *S*-alkyl groups could be equivalent (apart from possible conformational effects) with the unpaired electron in a σ^*-S—O orbital,

TABLE 1

RADICALS DETECTED BY ESR SPECTROSCOPY DURING THE REACTIONS OF TRIMETHYLSILOXYL OR TRIETHYLSILYL RADICALS WITH DIALKYL SULPHIDES AT ca. 213 K IN CYCLOPROPANE

Sulphide	Radicals detected with co-reactants	
	$\mathrm{Me_3SiOOSiMe_3}$[a]	$\mathrm{t\text{-}BuOOBu\text{-}t + Et_3SiH}$[b,c]
$\mathrm{Me_2S}$	$\mathrm{MeS\dot{C}H_2,\ Me_2\dot{S}OSiMe_3}$	$\mathrm{MeS\dot{C}H_2,\ Me^\bullet}$
$\mathrm{Et_2S}$	$\mathrm{EtS\dot{C}HMe,\ Et_2\dot{S}OSiMe_3}$	$\mathrm{EtS\dot{C}HMe,\ Et^\bullet}$
$\mathrm{i\text{-}Pr_2S}$	$\mathrm{i\text{-}PrS\dot{C}Me_2,\ i\text{-}Pr_2\dot{S}OSiMe_3}$	$\mathrm{i\text{-}PrS\dot{C}Me_2,\ i\text{-}Pr^\bullet}$
$\mathrm{t\text{-}Bu_2S}$	*d*	$\mathrm{Et_3Si^\bullet}$
$\mathrm{\overline{CH_2(CH_2)_3S}}$	$\mathrm{^\bullet\overline{CH(CH_2)_3S}}$	$\mathrm{^\bullet\overline{CH(CH_2)_3S},\ Et_3SiS(CH_2)_3\dot{C}H_2}$[e]
t-BuSMe	$\mathrm{t\text{-}BuS\dot{C}H_2,\ t\text{-}Bu(Me)\dot{S}OSiMe_3}$	$\mathrm{t\text{-}BuS\dot{C}H_2,\ t\text{-}Bu^\bullet}$
t-BuSPr-i	$\mathrm{t\text{-}BuS\dot{C}Me_2,\ t\text{-}Bu(i\text{-}Pr)\dot{S}OSiMe_3}$	$\mathrm{t\text{-}BuS\dot{C}Me_2,\ t\text{-}Bu^\bullet,\ Et_3Si^\bullet}$[f]

[a] A signal from a radical having the structure $\mathrm{^\bullet CH_2OSi\equiv}$ [3] was also detected in most systems. [b] Signals from persistent alkyl radicals were detected after prolonged photolysis, especially for the sulphides with bulky alkyl groups. [c] $\mathrm{[(R_2CH)_2S]}$ 0.5—2 *M*, $\mathrm{[Et_3SiH]}$ 2—5 *M*. [d] Apart from the spectrum due to $\mathrm{^\bullet CH_2OSi\equiv}$, some unidentified weak signals were present; no spectrum ascribable to $\mathrm{t\text{-}Bu_2\dot{S}OSiMe_3}$ was observed. [e] $a(2\mathrm{H}_\alpha)$ 22.1, $a(2\mathrm{H}_\beta)$ 28.4, $a(2\mathrm{H}_\gamma)$ 0.75 G. [f] $\mathrm{[t\text{-}Bu^\bullet]/[i\text{-}Pr^\bullet]} \geq 10$ at 213 K.

TABLE 2

ESR PARAMETERS FOR SULPHURANYL RADICALS OF THE TYPE II IN CYCLOPROPANE AT ca. 213 K

Radical	*g*-Factor	Hyperfine splittings (G)
$\mathrm{(CH_3)_2\dot{S}OSiMe_3}$	2.0076	a(6H) 7.7[a]
$\mathrm{(MeCH_2)_2\dot{S}OSiMe_3}$	2.0074	$a(2\mathrm{H}^1)$ 7.2, $a(2\mathrm{H}^2)$ 10.0
$\mathrm{(Me_2CH)_2\dot{S}OSiMe_3}$	2.0075	a(2H) 7.4[b]
$\mathrm{t\text{-}Bu(CH_3)\dot{S}OSiMe_3}$	2.0074	a(3H) 7.7
$\mathrm{t\text{-}Bu(Me_2CH)\dot{S}OSiMe_3}$	2.0074	a(1H) 5.2

[a] A further splitting into an even number (≥6) of lines, spacing ca. 0.2 G, was detected under high resolution and assigned to the nine protons of the $\mathrm{Me_3Si}$ group. The spectrum from $\mathrm{(CD_3)_2S}$ showed similar fine structure. [b] Central line broadens relative to the outer lines below 173 K, indicating non-equivalence of the two α-protons.

or the radical could be "T-shaped" with non-equivalent, but rapidly exchanging, apical and equatorial alkyl groups [1,4]. The non-equivalent methylene protons in $Et_2\dot{S}OSiMe_3$ and the temperature-dependence of the spectrum assigned to $i\text{-}Pr_2\dot{S}OSiMe_3$ (see Table 2) can be explained on the basis of either structure, although we favour the former of these.

A third type of behaviour, namely rapid S_H2 reaction at sulphur, which may or may not proceed by way of a discrete sulphuranyl radical intermediate, was observed by ESR spectroscopy when triethylsilyl radicals were generated in the presence of dialkyl sulphides. Photolysis of a cyclopropane solution containing the sulphide, di-t-butyl peroxide, and triethylsilane gave rise to overlapping spectra of the radicals $R_2\dot{C}H$ and I. At a given temperature, the ratio $[R_2\dot{C}H]/[I]$ increases as $[Et_3SiH]/[(R_2CH)_2S]$ increases indicating a competition between reactions 2 and 5.

$$t\text{-}BuO^{\cdot} + Et_3SiH \longrightarrow t\text{-}BuOH + Et_3Si^{\cdot} \qquad (5)$$

$$Et_3Si^{\cdot} + (R_2CH)_2S \longrightarrow Et_3SiSCHR_2 + R_2\dot{C}H \qquad (6)$$

The rates of silyldealkylation of dialkyl sulphides are sensitive to steric crowding at sulphur, for example t-butyl radicals are displaced much more rapidly from t-BuSMe or t-BuSPr-i than from $t\text{-}Bu_2S$ (see Table 1). Analogous S_H2 reactions between trimethylsilyl radicals and dialkyl selenides or tellurides have recently been detected by ESR spectroscopy [5].

References

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