

Low pressure pyrolysis of hexamethyldisilane: electron spin resonance identification of radical intermediates

Karel Mach^b, Graham P. Mills^a, J. Barrie Raynor^{a,*}

^a Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

^b Heyrovsky Institute of Physical Chemistry and Electrochemistry, Academy of Sciences of Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

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Abstract

Radicals produced in the pyrolysis of hexamethyldisilane at pressures below 1.5 Torr have been trapped in an adamantane matrix at 77 K and characterised by electron spin resonance spectroscopy. At 1 Torr, results were consistent with mechanisms proposed from gas-phase kinetic studies. At lower pressures the results suggest surface decomposition predominates, and they reveal a surprising feature of the mechanism that would not have been detected by the methods used in the earlier pyrolysis studies.

Keywords: Silicon; Radicals; Pyrolysis; Electron spin resonance

1. Introduction

There have been several studies of the kinetics and mechanism of the gas-phase pyrolysis of hexamethyldisilane, Me_6Si_2 , that have studied the remarkable sensitivity of the pyrolysis to reaction conditions. At high pressures of Me_6Si_2 , the main process is isomerisation to trimethylsilyl(dimethylsilyl)methane, $\text{Me}_3\text{SiCH}_2\text{Si}(\text{H})\text{Me}_2$, sufficiently cleanly for this to be a good method for synthesising the isomer [1,2]. At low pressures, however, the main products are trimethylsilane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane [3]. A mechanism, developed from pyrolysis studies [4,5] and a mercury-photosensitised decomposition [6], was proposed to account for these changes, and under all conditions pyrolysis was initiated by Si–Si bond rupture. The results of these studies have been reviewed in detail [7].

This paper describes further work on the pyrolysis of Me_6Si_2 using a technique in which radical intermediates generated by pyrolysis in a flow system at low pressures are trapped on a cold finger and subsequently

characterised by electron spin resonance (e.s.r) spectroscopy [8–10]. The radicals are usually co-condensed with adamantane at 77 K, which, even at this temperature, usually allows almost free rotation of the trapped radicals because of the large voids in the adamantane crystal lattice [11].

2. Experimental

Me_6Si_2 (Aldrich) was distilled under nitrogen at atmospheric pressure using a 24 in Vigreux column, and analysis by high field ^1H NMR (Bruker AMX250 FT-NMR) indicated the presence of approximately 0.15% of $\text{Me}_3\text{SiCH}_2\text{Si}(\text{H})\text{Me}_2$ as an impurity. Analysis with a Kratos Concept double-focusing mass spectrometer showed an M^+ peak for $\text{Me}_3\text{SiOSiMe}_3$ ($m/z = 162$) that was approximately 0.1% of the M^+ for Me_2Si_2 ($m/z = 146$), indicating only a slight siloxane impurity.

$\text{Me}_3\text{SiCH}_2\text{Si}(\text{H})\text{Me}_2$ was prepared by pyrolysis of Me_6Si_2 in a sealed Pyrex tube at a temperature of 710 K, and at a pressure of 10 atm, for 60 hours. The use of a sealed tube allowed the synthesis of only approximately 0.3 ml of $\text{Me}_3\text{SiCH}_2\text{Si}(\text{H})\text{Me}_2$ and this prevented purification by distillation. The sample of $\text{Me}_3\text{SiCH}_2\text{Si}(\text{H})\text{Me}_2$ thus contained 3% Me_2SiH , 5%

* Corresponding author.

unchanged Me_nSi_2 and traces of other unidentified products as well as approximately 1.2% siloxane impurity. Adamantane (Fluka) was recrystallised from freshly distilled cyclohexane and was sublimed in vacuo before use to remove trapped oxygen and residual cyclohexane.

A simple quartz and glass apparatus, described elsewhere [8], was evacuated to a base pressure of 10^{-5} Torr and the pyrolysis tube was heated to the desired temperature between 750 and 1000 K. The sample to be pyrolysed was admitted to the pyrolysis tube at pressures between 9×10^{-3} and 1.1 Torr (controlled by a metal needle-valve) and adamantane was introduced at a constant pressure of 8×10^{-2} Torr. Spectra were obtained with a Bruker ER 200D x-band e.s.r. spectrometer interfaced to a PC running Scientific Software Services EW package and g -values were determined by reference to diphenylpicrylhydrazine ($g = 2.0036$). The variable-temperature e.s.r. spectra were obtained by blowing cold N_2 produced by a Bruker B-VT-1000 variable-temperature unit into the cold finger Dewar in place of liquid N_2 .

3. Results

Pyrolysis of Me_nSi_2 at a pressure of 1 Torr produced a ten-line isotropic spectrum of radical A with $a(9\text{=H}) = 6.3$ G and with $g = 2.0030$ (shown in Fig. 1) at all pyrolysis temperatures studied between 780 and 970 K. The spectrum of radical A is readily assigned to the trimethylsilyl radical, $\text{Me}_3\text{Si}\cdot$, the spectrum of which has been reported [12,13] as having $a(9\text{=H}) = 6.28$ G and $g = 2.0031$. Warm-up experiments resulted in the disappearance of radical A at 135 K, leaving only a

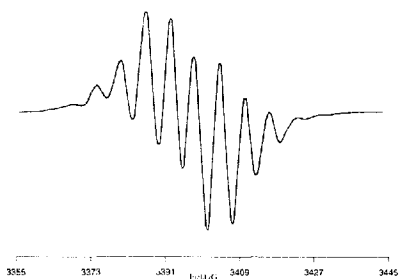


Fig. 1. First derivative e.s.r. spectrum of products (mostly radical A, $\text{Me}_3\text{Si}\cdot$) trapped in unreacted Me_nSi_2 at 77 K, formed during pyrolysis of Me_nSi_2 at 1 Torr and 930 K.

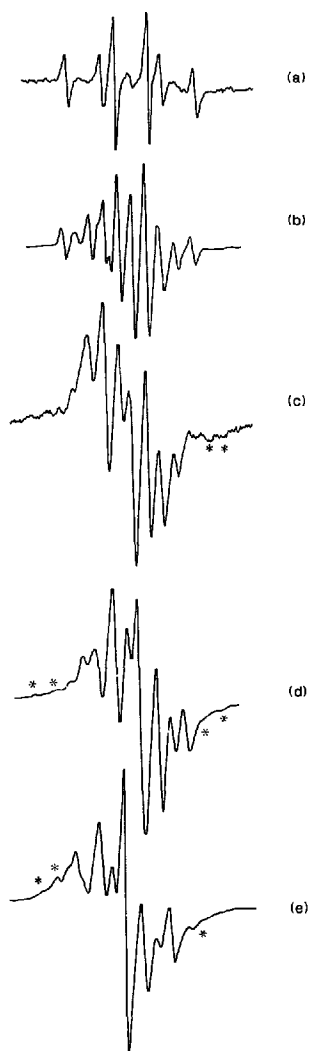


Fig. 2. E.s.r. spectrum of products, trapped in adamantane at 77 K, formed during pyrolysis of Me_nSi_2 at 2×10^{-2} Torr and at (a) 780 K, (b) 880 K, (c) 918 K, (d) 943 K, (e) 970 K. Lines marked with asterisk are unidentified.

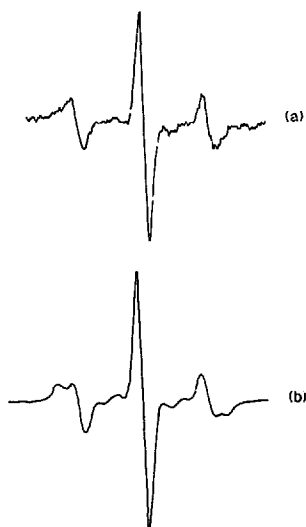


Fig. 3. Spectrum of Fig. 2(a) after warming to 165 K, showing radical B at (a) 165 K and (b) 77 K.

weak spectrum of radical B which was a triplet with $\alpha(2\equiv\text{H})$ approximately 21 G.

The pyrolysis of Me_2Si_2 at low pressures produced spectra, shown in Fig. 2(a)–(e), that were very different to those produced at higher pressures. Pyrolysis between 780 and 870 K gave a spectrum that contained signals from two radicals (B and C), the proportions of which did not vary within this temperature range. The signal of radical B was a triplet with $\alpha(2\equiv\text{H}) = 21.2$ G with $g = 2.0029$, and that of radical C was an isotropic triplet of doublets with $\alpha(\text{H}) = 15.3$ G and $\alpha(2\equiv\text{H}) = 20.8$ G, centred at $g = 2.0025$. Warming of the matrix to 165 K resulted in the disappearance of radical C, leaving the almost isotropic triplet shown in Fig. 3(a). Re-cooling of the matrix to 77 K gave the anisotropic spectrum (Fig. 3(b)), the outermost features of which were obscured in the mixtures by the lines of radical C. The strength of the radical B signal did not increase during the annealing process, indicating that radical B is formed during pyrolysis and is not the result of the decomposition of radical C (or radical A in Fig. 1).

The spectra obtained from pyrolysis between 880 and 970 K consisted of all three radicals, A, B and C, the proportions of which changed with the pyrolysis tem-

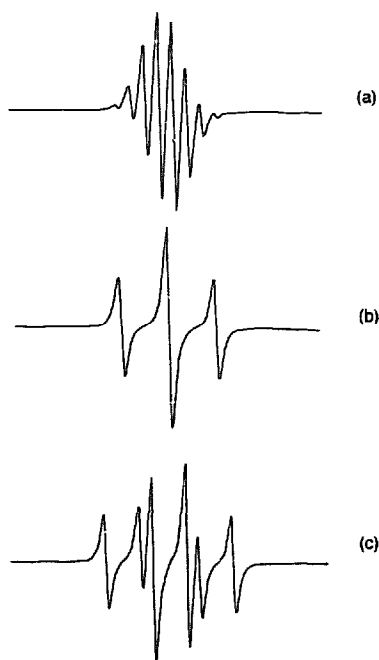


Fig. 4. Simulated isotropic e.s.r. spectra of radicals A, B and C.

perature. The relative amounts of the three radicals in the spectra observed for pyrolysis between 780 and 970 K were estimated by simulating the three radical signals using the parameters above. Lorentzian line shapes and line widths of 2.5 G, 3.0 G and 2.5 G respectively for A, B and C (Fig. 4). Combinations of the simulated spectra were then matched to the experimen-

Table 1
Proportions of radicals A, B and C estimated by simulation

Temperature (K)	Radical		
	A	B	C
780	—	0.2	1.0
880	1.6	1.2	1.0
918	1.8	1.7	1.0
943	2.1	2.4	1.0
970	2.2	2.8	1.0

tal spectra, the results of these estimations being shown in Table 1. Owing to the slight anisotropic nature of radical **B** at 77 K, the use of an isotropic triplet in the simulations results in an error in the estimated proportions of approximately 15%.

To determine if the decomposition of the $\text{Me}_2\text{SiCH}_2\text{Si(H)Me}_2$ impurity in the sample was responsible for the observed e.s.r signals, $\text{Me}_2\text{SiCH}_2\text{Si(H)Me}_2$ was pyrolysed under identical conditions to Me_6Si_2 .

The spectra obtained when the sample of $\text{Me}_2\text{SiCH}_2\text{Si(H)Me}_2$, as prepared, was pyrolysed were very similar to those obtained from Me_6Si_2 pyrolysis, except that they were much weaker. This suggests that $\text{Me}_2\text{SiCH}_2\text{Si(H)Me}_2$ does not decompose under the conditions used (it is known from the literature that $\text{Me}_2\text{SiCH}_2\text{Si(H)Me}_2$ is more thermally stable than Me_6Si_2 [4,5] and that radicals observed are the result of the decomposition of Me_6Si_2 only).

We propose that radical **C** is $\text{Me}_2\text{Si(H)CH}_2$, which has previously been observed as a spin-trapped product (the minor one, $\text{Me}_3\text{Si}^{\cdot}$ being the major trapped radical) [14] from the gas-phase photolysis of Me_3SiH and tentatively attributed to a weak spectrum observed during the reaction of Me_3SiH with cyclopropylbromide [15]. The triplet splitting of radical **C** is very close to the 20.88 G observed by Krusic and Kochi [13] for the Me_2SiCH_2 radical and the 20.22 G for the α -proton splitting of the Et_3SiCH_2 radical. Very similar hyperfine splittings are observed for the α -protons in the analogous Ge and Sn radicals, suggesting that the triplet splitting is due to an Si- CH_2 group rather than a Si-centred radical, for which the proton hyperfine splittings are much smaller than those observed for radical **C** (the α -H hyperfine splitting observed for the Si-centred MeSiH_2 radical is only 11.8 G) [16]. The doublet splitting of 15.3 G is small for a C-bonded H and this suggests that an Si-H group is responsible for this splitting, which is more consistent with the smaller splittings associated with Si- rather than C-bonded hydrogen [17,18].

The spectrum of radical **B** is anisotropic at 77 K, indicating that the radical is quite large, and is that which is expected from freely rotating $-\text{CH}_2$ units within randomly oriented radicals [19]. In this system, the two radicals most likely to be radical **B** are the $\text{Me}_2\text{Si}_2\text{CH}_2$ radical and the $\text{Me}_2\text{SiOSiMe}_2\text{CH}_2$ radical. These radicals have been studied in solution by Krusic and Kochi [17], and the observed spectra had very similar parameters ($a(\alpha) = 21.09$ G and 20.15 G, $a(\beta) = 0.78$ G and 0.24 G for $\text{Me}_2\text{SiOSiMe}_2\text{CH}_2$ and $\text{Me}_2\text{Si}_2\text{CH}_2$ respectively). Although the parameters of radical **B** are closer to those of $\text{Me}_2\text{Si}_2\text{CH}_2$ than $\text{Me}_2\text{SiOSiMe}_2\text{CH}_2$, it is not possible to positively identify radical **B** from the e.s.r spectrum. It is, however, possible to eliminate the $\text{Me}_2\text{CH}_2\text{SiCH}_2\text{Si(H)Me}_2$ radi-

cal, formed by hydrogen abstraction from the $\text{Me}_2\text{SiCH}_2\text{Si(H)Me}_2$ impurity, because the proportion of radical **B** is independent of the proportion of the isomer in the pyrolysis mixture.

4. Discussion

Gas-phase kinetic studies by a number of workers have shown that at low pressures the main products of the pyrolysis of Me_6Si_2 are trimethylsilane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. In these studies, $\text{Me}_2\text{Si}_2\text{CH}_2$, formed by rapid extraction of a hydrogen atom from Me_6Si_2 , very rapidly rearranges and decomposes to give $\text{Me}_2\text{Si}=\text{CH}_2$ and $\text{Me}_3\text{Si}^{\cdot}$, resulting in the predominance of the $\text{Me}_3\text{Si}^{\cdot}$ radical in the system. Thus, at a pressure of 1 Torr, the observation of $\text{Me}_3\text{Si}^{\cdot}$ as by far the most abundant radical is consistent with these earlier gas-phase kinetic studies and suggests that the pyrolysis is occurring mainly in the gas-phase.

The kinetic studies of the pyrolysis showed that rupture of the Si-Si bond in Me_6Si_2 is the initial step in the pyrolysis mechanism [7]. This reaction has Arrhenius parameters of $\log A = 17.2 \text{ s}^{-1}$ and $E_a = 337 \text{ kJ mol}^{-1}$, giving a half life of 162 s at 900 K and 24 s at 940 K and thus a small, but significant, amount of decomposition in the short residence time in the pyrolysis tube. This is consistent with the strength of the observed e.s.r signals. At 780 K the half life is 45 h (resulting in approximately $10^{-4}\%$ decomposition) and, with the small quantities of material used, should give a barely detectable e.s.r signal at best. However, the observed e.s.r signals are quite strong at this temperature.

The unexpectedly strong e.s.r signals at 780 K, the observation of $\text{Me}_2\text{Si(H)CH}_2$ and the large differences between the spectra observed for low and very low pressure pyrolyses suggest that an alternative decomposition pathway to that proposed in the earlier studies is being followed, especially at very low pressure.

At very low pressures, the $\text{Me}_2\text{Si(H)CH}_2$ radical is present in significant quantities at all temperatures studied and is predominant at the lowest temperatures. A possible source of this radical is the gas-phase isomerisation of the $\text{Me}_3\text{Si}^{\cdot}$ radical (the forward reaction in Eq. (1)). The reverse reaction has been studied in some detail [20] and has the Arrhenius parameters $\log A = 13.5 \text{ s}^{-1}$ and $E_a = 172 \text{ kJ mol}^{-1}$; also, from the bond strengths of the Si-H and C-H bonds [21] it was shown [22] that the $\text{Me}_2\text{Si(H)CH}_2$ radical was the less stable by some 25 kJ mol^{-1} with $E_a = 197 \text{ kJ mol}^{-1}$ for the reverse reaction in Eq. (1). The forward and reverse reactions in Eq. (1) thus have half lives, at 900 K, of 6 ms and 0.2 ms respectively. Thus, if gas-phase isomerisation was responsible, $\text{Me}_3\text{Si}^{\cdot}$ should be observed in large excess under all pyrolysis conditions. This

suggests that $\text{Me}_2\text{Si}(\text{H})\dot{\text{C}}\text{H}_2$ is formed by some other mechanism and is not the result of a gas-phase reaction.



The change in the proportions of $\text{Me}_3\text{Si}^\cdot$ and $\text{Me}_2\text{Si}(\text{H})\dot{\text{C}}\text{H}_2$ at different temperatures is very different to the change in relative rates of the forward and reverse reactions in Eq. (1) at the same temperatures, suggesting that there is little or no gas-phase isomerisation occurring between the formation of the radicals and their being trapped.

We believe that at very low pressures we are, not surprisingly, observing primarily surface-initiated decomposition with little contribution from gas-phase reactions. By far the weakest bond in Me_3Si_2 is the Si–Si bond and, as for the gas-phase studies, we would expect this bond to break initially to give adsorbed $\text{Me}_3\text{Si}^\cdot$ radicals. The observation of $\text{Me}_2\text{Si}(\text{H})\dot{\text{C}}\text{H}_2$ radicals suggests that the adsorbed $\text{Me}_3\text{Si}^\cdot$ radicals isomerise on the surface to form the less stable (at least in the gas-phase) $\text{Me}_2\text{Si}(\text{H})\dot{\text{C}}\text{H}_2$ radical. At very low pressure the proportions of these two radicals observed by e.s.r depend on the relative rates of desorption and isomerisation of the $\text{Me}_3\text{Si}^\cdot$ radicals, with desorption becoming more important at higher temperature. At higher pressures, any radical reaching the gas-phase will quickly react resulting, ultimately, in the rapid formation of $\text{Me}_3\text{Si}^\cdot$ radicals.

The uncertainty in the identity of radical **B** means that the fate of any $\text{Me}_3\text{Si}_2\dot{\text{C}}\text{H}_2$ radicals cannot be determined positively. If radical **B** is the $\text{Me}_3\text{Si}_2\dot{\text{C}}\text{H}_2$ radical, it is somewhat surprising that the products of the very rapid gas-phase decomposition of this radical, $\text{Me}_3\text{Si}^\cdot$ and $\text{Me}_2\text{SiCH}_2\dot{\text{S}}\text{i}(\text{H})\text{Me}_2$, are not observed at 780 K even though radical **B** is. It seems more likely that radical **B** is the $\text{Me}_3\text{SiOSiMe}_2\dot{\text{C}}\text{H}_2$ radical (which does not have the easy decomposition route of $\text{Me}_3\text{Si}_2\dot{\text{C}}\text{H}_2$ and is therefore more persistent) and that the $\text{Me}_3\text{Si}_2\dot{\text{C}}\text{H}_2$ has decomposed rapidly on the surface to give adsorbed $\text{Me}_3\text{Si}^\cdot$ radicals which then isomerise.

It is possible that the $\text{Me}_2\text{Si}(\text{H})\dot{\text{C}}\text{H}_2$ radical is formed as a result of a complex series of reactions on the surface of the pyrolysis tube and that the radical is not formed by isomerisation of the more stable $\text{Me}_3\text{Si}^\cdot$ radical.

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