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Preliminary communication

The rate constant for the self-reaction of trimethylsilyl radicals*

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In 1969 Thynne[1] reported a calculated rate constant for the combination of trimethylsilyl radicals, k_f, in the gas phase.

$$2\,Me_3Si^{\cdot} \underset{k_b}{\overset{k_f}{\rightleftarrows}} Me_3SiSiMe_3$$

The value calculated was $10^{5.5}$ mole^{-1} · cm^3 · sec^{-1}, *i.e.*, $10^{2.5}$ M^{-1} · sec^{-1}, which is inherently unreasonable in view of the fact that simple carbon centered radicals such as $CH_3^{\cdot}$, $CF_3^{\cdot}$ and $CCl_3^{\cdot}$ have rate constants for combination of ~ 10^{10} M^{-1} · sec^{-1} in the gas phase and ~ $2 \cdot 10^9$ M^{-1} · sec^{-1} in solution in solvents of normal viscosity. More significantly, we had already shown that the rate constants for the self-reactions of the structurally analogous t-butyl- and trimethyltin radicals were around $2 \cdot 10^9$ M^{-1} · sec^{-1} in solution[2] ($k_{Me_3C^{\cdot}} = 2.1 \cdot 10^9$ and $k_{Me_3Sn^{\cdot}} = 3.1 \cdot 10^9$ M^{-1} · sec^{-1}). It seemed improbable that k_f could be significantly below $2 \cdot 10^9$ M^{-1} · sec^{-1} in solution and we therefore set out to measure it.

The ESR spectrum of the trimethylsilyl radical has been detected by two groups of workers by photolyzing mixtures of trimethylsilane and di-t-butylperoxide in the cavity of an ESR spectrometer[3,4]. We have utilized the same system to generate the radicals and have measured their decay when the light was cut off on a Varian E-3 EPR spectrometer by the procedure of Weiner and Hammond[5]. That is, the light beam was repeatedly chopped by a rapidly rotating sectored disc. At the appropriate rotation speed a large number of identical radical decays were collected by a Fabri-Tek 1072 Signal Averager. Radical concentrations were determined relative to DPPH*** by the usual procedures[6]. Good second order decays were obtained. The bimolecular rate constants calculated from these decays are summarized in Table 1. Additional proof that the decay is indeed bimolecular is provided by the fact that the initial concentration of trimethylsilyl radicals, *i.e.*, the concentration under steady illumination, is proportional to the square root of the light intensity (see Figure 1).

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***DPPH = diphenylpicrylhydrazyl.

TABLE 1

RATE CONSTANTS FOR BIMOLECULAR DECAY OF PHOTOLYTICALLY GENERATED[a] TRIMETHYLSILYL RADICALS AT 25°

Relative light intensity[b] (%)	Number of decays collected	$[Me_3Si^{\bullet}] \cdot 10^7$ (*M*)	$k_f \cdot 10^{-9}$ $(M^{-1} \cdot sec^{-1})$[c]
100	1024	8.4	2.2
100	1024	8.4	1.9
100	1024	8.4	2.0
33	2048	5.5	1.2
13	4096	2.9	1.8
13	4096	2.9	2.0
13	4096	3.2	1.3
2.2	8192	1.3	3.6
2.2	8192	1.6	2.2
2.2	8192	1.3	2.5
0.7	16384	0.68	3.1
			Mean = 2.2±0.7

[a] $Me_3SiH/Me_3COOCMe_3$ 1/1 by volume with no other solvent present were distilled into the ESR tube and sealed under vacuum. Photolysis was by the light from an unfiltered 200 watt Osram super-pressure mercury lamp. [b] Intensity varied by inserting screens of known transmittance. Experiments done in a random order. [c] The steady-state concentration of t-butoxy radicals is very low because of their very fast reaction with Me_3SiH and, for this reason, the cross combination of $Me_3Si^{\bullet}$ and $Me_3CO^{\bullet}$ radicals is unimportant.

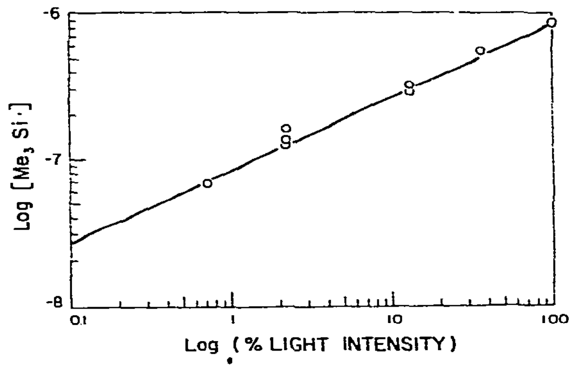

Fig.1. Trimethylsilyl radical concentration as a function of light intensity. The straight line has a slope of 0.5.

The measured rate constant for the combination of trimethylsilyl radicals is $2.2 \cdot 10^9$ $M^{-1} \cdot sec^{-1}$ which is right where we expect it to be. We therefore reexamined Thynne's calculations for possible errors. The thermodynamic expression which was used to calculate k_f is,

$$\log k_f = \log A_f = \log A_b + \Delta S/2.3R + 4.8$$

where k_f and A_f are in $mole^{-1} \cdot cm^3 \cdot sec^{-1}$ (it being assumed that the activation energy E_f is zero), A_b is in sec^{-1}, ΔS is the entropy change in $cal \cdot deg^{-1} \cdot mole^{-1}$ at 25° and

1 atmosphere pressure and the term 4.8 is a correction term for the change in the number of molecules between reactants and products[7]. The overall entropy change, ΔS, is given as -58.3 cal · deg^{-1} · mole^{-1} which seems much too large for a simple association of two radicals. The entropy value for the radical, $S^\circ[Me_3Si^{\cdot}] = 80.4$ cal · deg^{-1} · mole^{-1}, appears correct[7] but the value used for the disilane, $S^\circ[Me_3SiSiMe_3] = 102.5$ cal · deg^{-1} · mole^{-1} may be too low. Benson[7] gives $S^\circ[Me_3SiOSiMe_3] = 127.85$, $S^\circ[MeOMe] = 63.7$ and $S^\circ[C_2H_6] = 54.9$ cal · deg^{-1} · mole^{-1} from which we can estimate $S^\circ[Me_3SiSiMe_3] \approx 127.85 - 63.7 + 54.9 \approx 119$ cal · deg^{-1} · mole^{-1}. The overall entropy change is then, $\Delta S = 119 - 2(80.4) = -41.8$ cal · deg^{-1} · mole^{-1}, from which we calculate $k_f = 1.6 \cdot 10^6\ M^{-1} \cdot \text{sec}^{-1}$ which is still much too low.

Since the difficulty does not lie wholly in ΔS it would seem that the pre-exponential factor for the back reaction, A_b, must be wrong. Thynne[1] used a value for A_b of $10^{13.5}$ sec^{-1} this being the value reported by Davidson and Stephenson[8] in their study of the thermal decomposition of hexamethyldisilane in a static system at 523–555° and pressures of 0.2–0.8 mm Hg. However, an A factor of $10^{13.5}$ sec^{-1} for the simple fission of a molecule into two radicals is so much lower than the usual value[7] of $\sim 10^{16\pm1}$ sec^{-1} as to make it suspect. Davidson and Stephenson[8] found that the rate of formation of a rather complex mixture of products was directly proportional to the hexamethyldisilane concentration. The following non-chain homolytic reaction scheme was proposed.

$$Me_3SiSiMe_3 \rightarrow 2Me_3Si^{\cdot} \qquad (1)$$

$$Me_3Si^{\cdot} + Me_3SiSiMe_3 \rightarrow Me_3SiH + Me_3SiSiMe_2CH_2^{\cdot} \qquad (2)$$

$$Me_3Si^{\cdot} + Me_3SiSiMe_3 \rightarrow Me_4Si + Me_3SiSiMe_2^{\cdot} \qquad (3)$$

$$Me_3Si^{\cdot} + Me_3SiSiMe_2CH_2^{\cdot} \rightarrow Me_3SiSiMe_2CH_2SiMe_3 \qquad (4)$$

$$Me_3SiSiMe_2^{\cdot} + Me_3SiSiMe_2CH_2^{\cdot} \rightarrow Me_3SiSiMe_2CH_2SiMe_2SiMe_3 \qquad (5)$$

Steady state treatment of this scheme yielded k_1 (which should be equivalent to k_b), the variation with temperature of which could be described by the relation $k_1 = 10^{13.5\pm1.0} \exp(-67300 \pm 2200)/RT$ sec^{-1}

The assumption in the above scheme that trimethylsilyl radicals disappear only by reactions 2, 3[★] and 4 is not necessarily correct since reaction 2 (and 3[★]) will have a high activation energy. Davidson and Stephenson[8] estimate that reaction 2 is 17 kcal/mole endothermic and that it has an activation energy of at least 20 kcal/mole. If we accept this activation energy and assume that A_2 has the "normal" value for a pre-exponential factor for a hydrogen atom abstraction, *i.e.*[7], $10^{8.5}\ M^{-1} \cdot \text{sec}^{-1}$ we can calculate the steady state concentration of trimethylsilyl radicals. Thus, at 800°K and at a disilane pressure of 0.5 mm ($\sim 10^{-5}\ M$) the rate of reaction 2 is $= k_2[Me_6Si_2][Me_3Si^{\cdot}] = 10^{8.5} \exp(-20000/4.6 \cdot 800) \cdot 10^{-5}[Me_3Si^{\cdot}] = 1.3 \cdot 10^{-2}[Me_3Si^{\cdot}]\ M \cdot \text{sec}^{-1}$. This rate must be approximately equal to the measured rate of product formation or disilane

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[★] Reaction 3 is rather unlikely as there is no authentic case of homolytic substitution at an unstrained sp^3 hybridized carbon atom [9].

decomposition which is given by $k_1\,[\mathrm{Me_6Si_2}] = 10^{13.5}\exp(-67300/4.6\cdot 800)10^{-5} = 1.6\cdot 10^{-10}\ M\cdot\mathrm{sec}^{-1}$. The steady state concentration of $\mathrm{Me_3Si^{\cdot}}$ radicals is therefore equal to $1.6\cdot 10^{-10}/1.3\cdot 10^{-2} = 1.2\cdot 10^{-8}\ M$. This is the radical concentration that is required to give the observed rate of product formation.

Chemical intuition and our present results in solution indicate that in the gas phase $k_f \approx 10^{10}\ M^{-1}\cdot\mathrm{sec}^{-1}$. The rate of the self-reaction of trimethylsilyl radicals will therefore be $k_f[\mathrm{Me_3Si^{\cdot}}]^2 = 10^{10}(1.2\cdot 10^{-8})^2 = 1.4\cdot 10^{-6}\ M\cdot\mathrm{sec}^{-1}$ which is 10^4 times as large as the measured rate of decomposition of the disilane, $k_1\,[\mathrm{Me_6Si_2}]$. These simple calculations imply that the principal reactions occurring under Davidson and Stephenson's experimental conditions was decomposition of the disilane and recombination of trimethylsilyl radicals. This possibility had, however already been checked and eliminated by Davidson and Stephenson for a closely analogous compound, ethylpentamethyldisilane[10]. If a dissociation-combination situation existed for this compound one would expect to find $\mathrm{Me_6Si_2}$ and $\mathrm{(EtMe_2Si)_2}$ at temperatures below those at which other decomposition products were formed. However, temperatures high enough to cause dissociation were also high enough for products to be formed indicative of an abstraction reaction analogous to reaction 2. We are therefore left with an unusually low A factor for reaction 1 unless it is assumed that ethylpentamethyldisilane behaves differently to hexamethyldisilane★.

In conclusion, it seems likely that the activation energy of 67.3 kcal/mole found by Davidson and Stephenson for the decomposition of hexamethyldisilane will be approximately equal to E_1 (and hence, to $D(\mathrm{Me_3Si{-}SiMe_3})$). However, for as yet undetermined reasons, their pre-exponential factor of $10^{13.5}\ \mathrm{sec}^{-1}$ is probably low, perhaps by as much as a factor of 10^4.

Further quantitative kinetic studies on the decay of other organometallic radicals will be fully reported in the near future.

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★Possibly the methylene hydrogens of the ethyl group are more susceptible to abstraction by silyl radicals than methyl hydrogens or perhaps decomposition occurs in part by an intramolecular reaction.