action. Alternatively, it is quite possible that electron or radical transfer from the pyrimidine to surfactant interferes with the chain reaction thereby contributing to the decrease in the overall base destruction yield. Clearly the present data do not allow distinction among these possibilities.

Disappearance of Silyl Radicals in Silane. A Flash Photolysis–Electron Spin Resonance Kinetic Study[1]

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Abstract: Bimolecular self-reaction has been established as the dominant path for the disappearance of silyl and trimethylsilyl radicals dissolved in the corresponding silane. Rate constants were determined for trimethylsilyl radical self-reaction over the temperature range +20 to −82°. The activation parameters deduced from the temperature dependence of the rate constant and the rate constants themselves are typical for group IV radicals. Similar rate constants were found for the self-reaction of silyl radicals at −120 and −150°. Product studies indicate that dimerization is the principal self-reaction mechanism for trimethylsilyl radicals. A chain-carrying displacement of hydrogen atoms from a silane by a silyl or trimethylsilyl radical is not an important reaction under the present reaction conditions. The formation of disilane, the dimer of SiH_3, and the similarity of the self-reaction rates of silyl and trimethylsilyl radicals strongly suggest that direct dimerization is the mechanism for silyl radical self-reaction in solution.

The nature of the reactive intermediates formed upon pyrolysis and photolysis of silane, SiH_4, has been controversial for nearly 40 years.[2] Agreement has still not been reached on the question whether gas-phase pyrolysis of silane produces silylene, SiH_2, and molecular hydrogen, or alternatively silyl radicals, SiH_3, and hydrogen atoms. Mechanisms have been suggested involving either primary process to account for the formation of the observed products, disilane and molecular hydrogen.

Mechanism A $\quad SiH_4 \longrightarrow SiH_2 + H_2 \quad (1)$

$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \quad (2)$

Mechanism B $\quad SiH_4 \longrightarrow SiH_3 + H \quad (3)$

$H + SiH_4 \longrightarrow SiH_3 + H_2 \quad (4)$

$SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H \quad (5)$

$2SiH_3 \longrightarrow Si_2H_6 \quad (6)$

To shed light on the interesting question, by what reaction paths do silyl radicals in silane solution disappear, it was decided to undertake a kinetic study. For the production of silyl radicals the convenient procedure of Krusic and Kochi was employed.[3] *tert*-Butyl peroxide is photolyzed to *tert*-butoxy radicals which abstract hydrogen atoms from silanes thus producing silyl radicals in solution.

The kinetic technique is similar to that developed by Weiner and Hammond.[4] The photolysis of *tert*-butyl peroxide is carried out with a modulated light source in order to facilitate signal averaging. Interference from signals due to long-lived free radicals is eliminated by use of a phase-sensitive detector to tune the detector response to the photolysis light frequency. Reaction mixtures thermostated with a gas stream are irradiated *in situ* in the microwave cavity of an electron spin resonance spectrometer.

In this manner growth and decay curves for the light-induced esr signal were collected and averaged. A typical decay curve for SiH_3 is shown in Figure 1. A similar technique has been used by Frangopol and Ingold[5a] and Watts and Ingold[5b] to measure the self-reaction rates of several organosilyl radicals. The apparatus for the present experiments has been described in connection with studies by Levanon and Weissman of the formation and decay of excited triplet molecules.[6,7]

While the goal of this investigation was to determine the mechanism for the disappearance of silyl radicals in silane solution, the mechanism cannot be determined from kinetic studies alone. Establishment of the rate law does not permit a choice between (1) a radical chain mechanism including disilane formation by *both* a chain-carrying "displacement"[8] *and* a bimolecular chain-terminating step; and (2) a nonchain process in which self-reaction of silyl radicals is the only process yielding disilane.

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[1] This work has been carried out with financial support under contract from the U. S. Atomic Energy Commission. This is AEC Technical Report No. COO-1713-30.

[2] (a) For a review of the investigation of silane decomposition, see P. P. Gaspar and B. J. Herold, "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1971, Chapter 13. Important work has appeared since this reference went to press: (b) M. A. Ring, M. J. Puentes, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **92**, 4845 (1970); (c) P. John and J. H. Purnell, *J. Organometal. Chem.*, **29**, 236 (1971).

[3] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3938 (1969).

[4] (a) S. Weiner and G. S. Hammond, *ibid.*, **90**, 1659 (1968); (b) *ibid.*, **91**, 986 (1969).

[5] (a) P. T. Frangopol and K. U. Ingold, *J. Organometal. Chem.*, **25**, C9 (1970); (b) C. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).

[6] H. Levanon, *Chem. Phys. Lett.*, **9**, 257 (1971).

[7] H. Levanon and S. I. Weissman, *J. Amer. Chem. Soc.*, **93**, 4309 (1971).

[8] It should be noted that Professor Ring envisions silyl radicals inserting into an Si–H bond of silane while losing a hydrogen atom, a process which might be described as an insertion–elimination, in contrast with simple displacement.

insertion–elimination $\quad \cdot SiH_3 + SiD_4 \longrightarrow SiH_2DSiD_3 + H$

displacement $\quad \cdot SiH_3 + SiD_4 \longrightarrow SiH_3SiD_3 + \cdot D$

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO$$

$$(CH_3)_3CO + SiH_4 \xrightarrow{k_2} (CH_3)_3COH + SiH_3$$

$$\begin{array}{c}\text{chain}\\ \text{mechanism}\\ \text{B}\end{array}\left\{\begin{array}{r}SiH_3 + SiH_4 \xrightarrow{k_3} Si_2H_6 + H\\ H + SiH_4 \xrightarrow{k_4} SiH_3 + H_2\end{array}\right\}\ \text{chain-carrying steps}$$

$$2SiH_3 \xrightarrow{k_5} Si_2H_6 \quad \text{chain termination}$$

$$\text{nonchain mechanism A} \quad 2SiH_3 \xrightarrow{k_5} Si_2H_6$$

It is clear that if $k_4 \gg k_3$, then the silyl radical concentration will be attenuated *only* by the chain-termination step. It is believed that k_2 and k_4 are considerably larger than k_3.[2b,3,9,10] Thus a bimolecular rate law is predicted for the disappearance of silyl radicals by any combination of the above mechanisms, independent of the chain length of the radical displacement.

The operation of a chain reaction can, however, be diagnosed by the ratio of disilane to *tert*-butyl alcohol formed as reaction products. Nonchain mechanism A predicts a 2:1 ratio $(CH_3)_3COH$ to Si_2H_6. If chain mechanism B is important the ratio should be very small, depending of course on the relative rates of the steps designated by k_3 and k_5. An estimate has been made for the chain length in the gas phase at *ca.* 300 Torr and 328° to be *ca.* $10^{11.5}$ by Ring, Puentes, and O'Neal.[2b] The rate constant for dimerization of silyl radicals should also be helpful in assessing the contribution of a chain mechanism to the reaction in solution. A very *slow* dimerization of silyl radicals in the gas phase was postulated by Ring and coworkers.[2b] Since the displacement designated by k_3 is believed by Ring to have an activation energy of *ca.* 14 kcal/mol[2b] it is clear that the displacement is unlikely to compete with dimerization at any readily accessible conditions of temperature or concentration, *if* the dimerization is as rapid as alkyl radical recombination.

Experimental Section

Materials. The sources of the compounds used, their nominal purity, and the means employed for further purification, if any, are: silane, Matheson Gas Products, semiconductor grade, 99.5%; ethane, Phillips Petroleum Co., research grade, 99.98%; trimethylsilane, Pierce Chemical Co., no purity given but no volatile impurities detected by gas chromatographic analysis; di-*tert*-butyl peroxide, Matheson Coleman and Bell, practical, purified by fractional distillation at 90 Torr (a middle fraction boiling at 52° was taken);[11] *tert*-butoxytrimethylsilane ($(CH_3)_3SiOC(CH_3)_3$), synthesized from trimethylchlorosilane and *tert*-butyl alcohol by the method of Gerrard and Kilburn[12] and purified by fractional distillation.

Sample Preparation. All irradiations, both for kinetic runs and product studies, were carried out in Suprasil quartz tubes: 4-mm o.d., 3-mm i.d., *ca.* 10 cm in length. The Suprasil tubes were attached to 12-mm o.d. quartz tubes of *ca.* 8-cm length which served as expansion bulbs. Sample tubes for silane were equipped with break-seal tubes for reattachment to a vacuum line. Reaction mixtures of volumes 0.1 to 0.5 ml were employed, the smaller volumes used when entire reaction mixtures were subjected to vapor-chromatographic analysis and the larger volumes when aliquoting was appropriate.

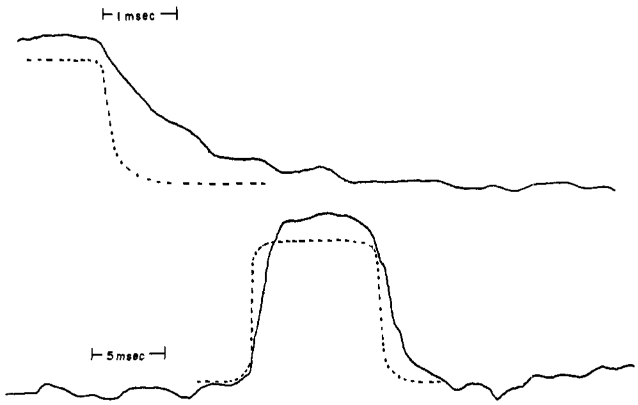

Figure 1. Typical growth and decay curves for the $\cdot SiH_3$ radical at −150°. Solid line represents radical concentration (8000 scans) and dotted line represents light intensity.

After careful baking of the sample tubes, the required amount of *tert*-butyl peroxide was added from a microsyringe. Then the sample tube was attached to a vacuum line and evacuated to 10^{-5} Torr by several freeze–pump–thaw cycles. The required amount of a silane and, when used, ethane solvent was frozen into the sample tube, after which the tube was sealed with an oxygen-gas flame. The reaction mixtures were thoroughly mixed prior to irradiation by agitation of the sample tubes. To maintain subatmospheric pressures within tubes containing silane, the inverted sample tubes were suspended in isopentane slush baths (−157°) and the contents thoroughly mixed in the expansion bulb while held in the slush bath. Sealed tubes containing silane were stored in liquid nitrogen until irradiation.

Irradiations. All kinetic measurements were carried out by irradiation directly in the cavity of a Varian E-3 esr spectrometer. The sample tube (and thermocouple when in use) were suspended in an unsilvered quartz dewar whose temperature was maintained by a stream of cold nitrogen gas from a liquid nitrogen "boiler." A 150-W xenon lamp (Eimac R-150-2) controlled by a variable on–off time pulser was used as the photolysis light source. The rise and fall time of the lamp is *ca.* 10^{-5} sec. Light and dark periods of 10^{-4} to 10 sec duration can be produced. The lamp was also used for constant illumination.

Recording of Data. Esr spectra of photochemically generated short-lived free radicals were obtained in two ways. The characteristic ten-line spectrum of the trimethylsilyl radical[13] (with 6.2 ± 0.2 G splitting) was obtained over a wide temperature range (−87–20°) on the E-3 recorder by sweeping the magnetic field under steady illumination. The characteristic four line silyl radical spectrum[3] (1:3:3:1 quartet 7.8 ± 0.2 G splitting) was obtained in the temperature range −120 to −160° by feeding the signal output of the E-3 into a lock-in amplifier tuned to the modulation frequency of the photolysis light source, while slowly sweeping the magnetic field. The output of the phase-sensitive detector was in turn fed back into the external input of the E-3 recorder. The reference signal for the lock-in amplifier was provided directly from the lamp power supply or from a photodiode positioned in front of the esr cavity. When the derivative of susceptibility *vs.* field was recorded under steady illumination, only after several hours did the spectra contain peaks due to long-lived radicals in addition to the silyl radical spectra.

Kinetic measurements were made utilizing the rapid storage capability of a capacitative storage device (PAR waveform eductor) or a computer of average transients (Varian CAT). The magnetic field of the E-3 was fixed to give the maximum signal intensity from the largest peak in the esr spectrum of the silyl radical of interest. The signal intensity as a function of time during a light on, light off cycle was averaged and stored for many cycles by triggering successive sweeps of the waveform eductor (or CAT) at the same point in every cycle. Since the line shapes and half-line widths of the esr signals obtained from the radicals studied in this investigation were found to be invariant to changes in radical concentration, the signal height could be assumed to be linearly proportional to the radical concentrations. Thus the signals

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(9) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968).

(10) H. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964).

(11) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956).

(12) W. Gerrard and K. S. Kilburn, *ibid.*, 1536 (1956).

(13) S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organometal. Chem.*, **16**, P36 (1969).

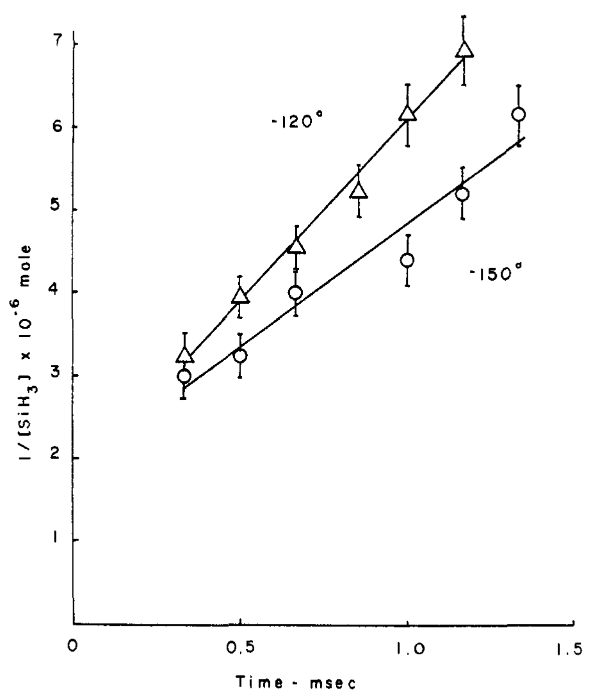

Figure 2. Second-order kinetic plots for $\cdot SiH_3$ radical, reciprocal concentration *vs.* time.

extracted from the waveform eductor into an X-Y recorder represent growth and decay curves for the silyl radicals. A typical curve is shown in Figure 1. These kinetic techniques have been developed by Weissman and Levanon.[6,7]

The absolute concentrations of radicals were determined by comparison of the total double-integrated peak area of the radical esr derivative signal with that of a standard diphenylpicrylhydrazyl–potassium chloride mixture which was in turn calibrated against a solution of diphenylpicrylhydrazyl (DPPH) in 1,2-dichloroethane. To avoid problems associated with a variation in conditions, a capillary tube containing a known concentration of DPPH was attached to the sample tube containing the silyl radical so that measurements of both radical signals could be carried out at nearly the same time under similar cavity conditions. Since the DPPH and silyl radical signals appear at almost the same field position ($g_{DPPH} = 2.00354$, $g_{SiMe_3} = 2.0031$) the light-induced silyl radical signal was recorded using the phase-sensitive detector and modulated light source, and the DPPH signal was recorded without sample irradiation. For comparison with the DPPH signal the silyl radical signal was converted to that obtained under constant illumination, the correction factor having been obtained in a separate experiment utilizing identical conditions and instrumental settings in the absence of DPPH. This method for obtaining absolute radical concentrations gives a probable error of *ca.* 25%.

Calculation of Rate Constants. It is assumed that the reaction of *tert*-butoxy radicals with silanes is fast compared to the decay of the silyl radicals.[5b,14] The decay curves were analyzed according to the following mechanism.

$$BOOB \xrightarrow{h\nu} 2BO\cdot$$

$$BO\cdot + R_3SiH \xrightarrow{\text{fast}} BOH + R_3Si\cdot$$

$$2R_3Si\cdot \xrightarrow{k_t} R_3SiSiR_3$$

$$B = (CH_3)_3C;\ R = H, CH_3$$

$$-d[R_3Si\cdot]/dt = 2k_t[R_3Si\cdot]^2$$

Upon integration

$$\frac{1}{[R_3Si\cdot]} = \frac{1}{[R_3Si\cdot]_0} + 2k_t t$$

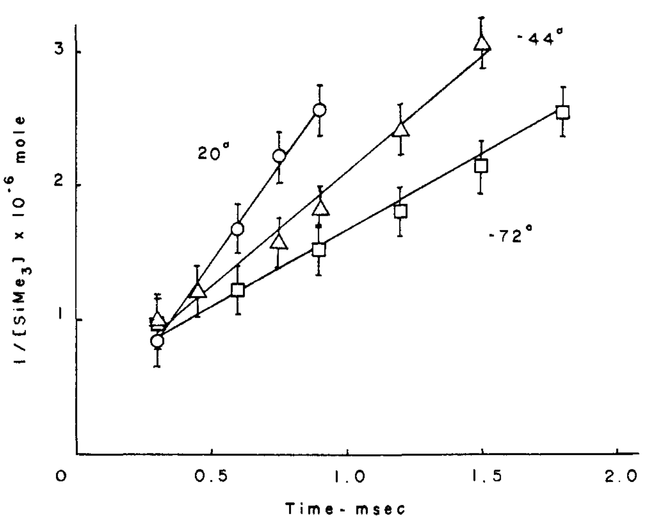

Figure 3. Second-order kinetic plots for the $\cdot SiMe_3$ radical, reciprocal concentration *vs.* time.

Typical kinetic plots are shown in Figures 2 and 3. Calculated rate constants are given in Table I. Data for the trimethylsilyl radical are given for comparison with the unsubstituted silyl radical. The rate constant obtained for the dimerization of trimethylsilyl is in good agreement with the previously published value of Ingold and coworkers.[5] That the decay of silyl as well as trimethylsilyl radical is a second-order reaction is indicated by the linear dependence of the logarithm of the steady-state radical signal on the logarithm of the light intensity under steady illumination with slope $^1/_2$,[5a] shown in Figures 4 and 5.

Table I. Rate Constants for Self-Reactions of Silyl Radicals

Species	Temp, °C	Medium[a]	$2k_t \times 10^9$ M^{-1} sec^{-1} [b]
$\cdot SiH_3$	−120	A	4.5 ± 0.3
	−120	A	4.1 ± 0.2
	−150	A	2.7 ± 0.3
$\cdot Si(CH_3)_3$	20	B	2.9 ± 0.1
	20	B	3.1 ± 0.2
	0	B	2.8 ± 0.1
	−23	B	2.6 ± 0.3
	−38	B	1.8 ± 0.1
	−44	B	1.7 ± 0.1
	−60	B	1.7 ± 0.1
	−72	B	1.1 ± 0.1
	−82	B	1.3 ± 0.1

[a] B is $HSi(CH_3)_3$:$(CH_3)_3COOC(CH_3)_3$ = 5:1 v/v; A is SiH_4:$(CH_3)_3COOC(CH_3)_3$:CH_3CH_3 = 1:1:0.5 v/v. [b] Rate constants calculated from rate law $-d[\cdot SiR_3]/dt = 2k_t[\cdot SiR_3]^2$.

From the variation of the rate constant for dimerization of trimethylsilyl radicals with temperature over the range −87 to 20° an activation energy and preexponential factor have been derived from a plot of the Arrhenius relationship $\log k = \log A - E_a/2.3RT$. The plot shown in Figure 6 gives values $E_a = 1.0 \pm 0.2$ kcal, $\log A = 9.9 \pm 0.2$. Unfortunately, the temperature range covered by the unsubstituted silyl radical experiments was too small to permit the calculation of accurate activation parameters. The "Arrhenius plot" from two points at −120 and −150° gives $\log A = 10.2 \pm 0.5$ and $E_a = 0.6 \pm 0.6$ kcal.

Product Analysis. After irradiation trimethylsilane–*tert*-butyl peroxide reaction mixtures were cooled to −78°, and the expansion bulb was sealed off and separated from the liquid products. The expansion bulb was broken in the inlet chamber of a gas chromatograph and the gaseous products analyzed on a 10-ft by 0.25-in. molecular sieve 5A column (40–60 mesh) at room temperature. These chromatographic conditions were chosen in order to detect hydrogen. None was found. A yield of hydrogen greater than 5% based on consumed peroxide would have been detected. The liquid products were injected with a precooled microsyringe onto a

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[14] S. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 91, 2182 (1969).

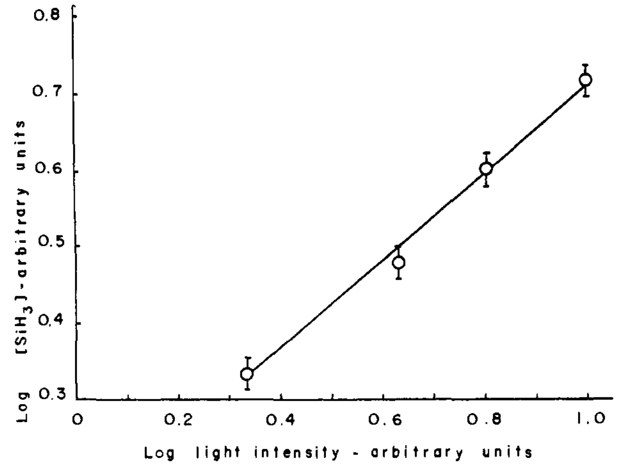

Figure 4. Dependence of the $\cdot SiH_3$ radical concentration upon light intensity; slope is 0.58 ± 0.04.

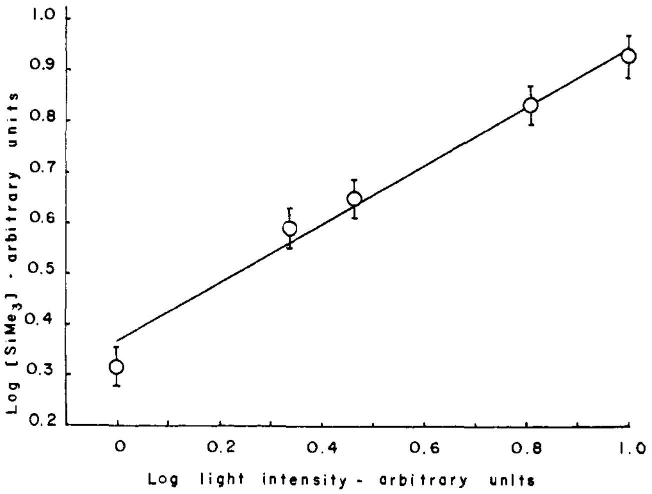

Figure 5. Dependence of the $\cdot SiMe_3$ radical concentration upon light intensity; slope is 0.57 ± 0.04.

30 ft × 0.50 in. column of 20% silicone oil SF96 on acid- and base-washed and silanized diatomaceous earth (Anakrom ABS) operated at 80° with a helium carrier gas flow rate of 60 ml/min. The components of the reaction mixture detected and their retention times were *tert*-butyl alcohol (5.9 min), *tert*-butoxytrimethylsilane (15.2 min), hexamethyldisilane (17.9 min.), and *tert*-butyl peroxide (18.8 min). No other peaks were observed in the vapor chromatograms using several different stationary phases. The products were identified by comparison of retention times with samples of authentic materials and by the nmr spectra of the individual products trapped from the effluent of the vapor chromatograph. The relative sensitivities of the thermal conductivity detector to the major components of the reaction mixture were determined from authentic mixtures of known composition. The observed relative sensitivities are 1:1.0 ± 0.1:1.0 ± 0.1 for *tert*-butyl peroxide, hexamethyldisilane, and *tert*-butyl alcohol, respectively.

In order to determine the relative quantum yield of disilane formation from the reaction stoichiometry and also to shed light on the source of the unexpected product *tert*-butoxytrimethylsilane, a number of identical 3.5:1.5 trimethylsilane-*tert*-butyl peroxide reaction mixtures, 0.5 ml each, were prepared and irradiated together for varying periods of time at room temperature using a Hanovia medium-pressure 450-W mercury arc as the light source. The results are given in Figure 7.

Silane-*tert*-butyl peroxide and silane-ethane-*tert*-butyl peroxide reaction mixtures were expanded, after irradiation into the vacuum line and aliquoted into several small Pyrex tubes for vapor chromatographic analysis. Care was taken to avoid fractionation of the reaction mixture during the transfer and aliquoting operations.

The aliquots were analyzed by vapor chromatography employing two columns connected in series with the thermal conductivity detector using two switching valves. By manipulation of the valves, lower boiling components of an aliquot were passed through both columns and then again through the first column before reaching the thermal conductivity detector. The higher boiling components of the same aliquot could be directed to pass through the first column only. This shunting arrangement permitted separation of the low-boiling components silane and disilane while also allowing the detection of higher boiling components, all under isothermal conditions. The first column was 20 ft × 0.25 in. 20% silicone oil SF-96 on acid- and base-washed and silanized diatomaceous earth (Anakrom ABS 40–50 mesh). The second column was 20 ft × 0.25 in. 60:20:100 by weight diethyl phthalate to Silicone Oil DC 710 to Anakrom ABS, 40–50 mesh. With a 60-ml/min helium carrier gas stream and 49° column temperature, the products detected and their retention times were: silane (8.6 min on columns A + B + A), disilane (13.8 min on columns A + B + A), *tert*-butyl alcohol (15.8 min on column A only), *tert*-butoxysilane (tentatively identified) (18.0 min on columns A only). No hydrogen was detected. Under these conditions a 10% yield of hydrogen would have been found. Relative sensitivities of the thermal conductivity detector toward disilane and *tert*-butyl alcohol were found to be 1:2.0 ± 0.2. The relative yields of disilane and *tert*-butyl alcohol were 1:2.6 ± 0.6, after 1.5 hr ir-

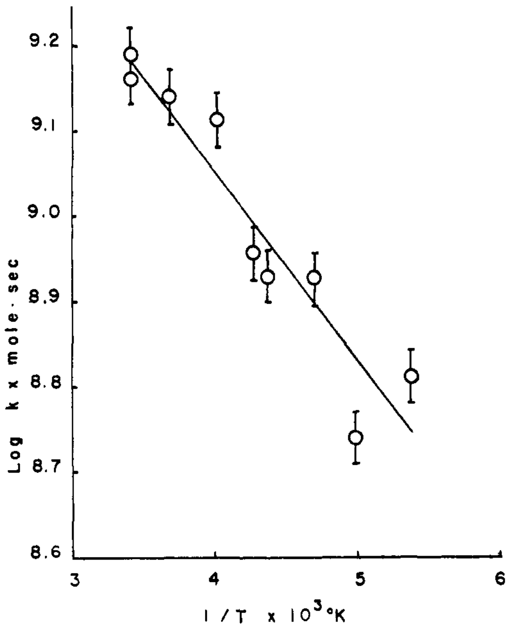

Figure 6. Arrhenius plot for the $\cdot SiMe_3$ radical, log of rate constant *vs.* reciprocal temperature.

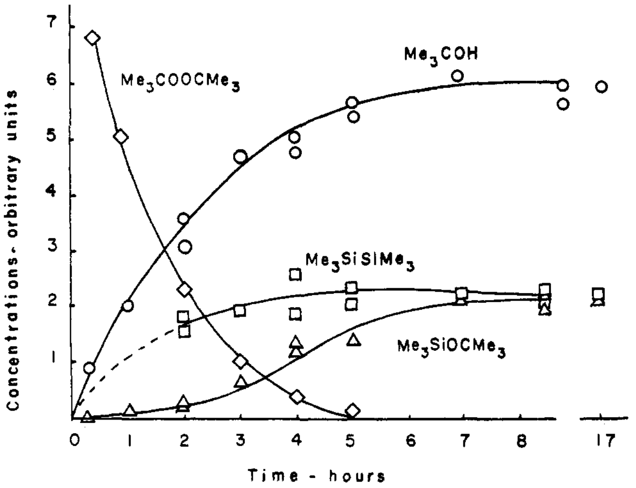

Figure 7. Composition of reaction mixture as a function of irradiation time. Initial composition 3.5:1.5, $Me_3SiH-Me_3COOCMe_3$.

radiation time. The solubility of *tert*-butyl peroxide in silane and silane–ethane mixtures is low at the temperatures employed (−120 to −150°). Thus there is usually a small amount of solid peroxide in the sample tube. Unless the solid is shielded from irradiation, the ratio of *tert*-butyl alcohol to disilane increases above 3. The ratio did not depend on the amount of ethane diluent, however.

Discussion

From rate measurements on the disappearance of silyl radicals at various temperatures, it was hoped to determine the order of reaction and the activation parameters. The disappearance of trimethylsilyl radicals is known to be a second-order process from the work of Frangopol and Ingold.[5a] We determined the temperature dependence of the rate constant in order to deduce the activation parameters, and in order to compare the reactions of silyl radicals in silane with those of trimethylsilyl radicals in trimethylsilane.

The decay of both silyl and trimethylsilyl radicals in the presence of a large excess of the corresponding silane is a rapid reaction, second order in the concentration of silyl radicals. That these reactions are indeed second order is indicated by the satisfactory second-order decay plots (Figures 2 and 3) together with the dependence of the steady-state radical concentration under constant illumination upon the square root of the light intensity (Figures 4 and 5).[15] When the data of Figures 2 and 3 are plotted as *first-order* decays, greater deviations from linearity result than those displayed by these figures.

Frangopol and Ingold have measured the rate of self-reaction of trimethylsilyl radicals at 25° and obtained a rate constant $2.2 \pm 0.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$,[5a] later corrected to $5.5 \pm 0.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[5b] The rate constant obtained in our experiments at 20°, $3.0 \pm 0.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, is in satisfactory agreement with the published result. From the temperature dependence of the rate constant (Figure 6) we have obtained the Arrhenius activation parameters for trimethylsilyl radical self-reaction; $\log A = 9.9 \pm 0.2$ and $E_a = 1.0 \pm 0.2$ kcal/mol. The efficiency of self-reaction is indicated by comparison of $\log A$ with that for methyl radicals in the *gas phase* $\log A = 10.3$.[16]

The rate constant for self-reaction of silyl radicals is larger than that for trimethylsilyl radicals (Table I). While no accurate activation parameters could be derived from our limited data, it is clear that $\log A$ lies between 9.7 and 10.7 $M^{-1}\ \text{sec}^{-1}$ and E_a is very small (<1.0 kcal/mol). Thus the preexponential factor for the self-reaction of both silyl and trimethylsilyl radicals is some four orders of magnitude greater than has been previously estimated for the process in the gas phase.[2b,17] It is clear that the self-reaction of silyl radicals in solution fits into the pattern of other group IV radical self-recombinations.[4,5,18]

The low activation energies observed for the self-reactions of silyl and trimethylsilyl radicals suggest that caution be exercised in the comparison of the gas- and liquid-phase reaction rates. Even when the mechanisms of gas- and liquid-phase reactions are identical, and they may indeed differ due to a variety of solvent effects,[19] meaningful comparisons of reaction rates may by frustrated for highly reactive species by the dominance by encounter control of the reaction rate in the liquid phase.[20–22]

Having established that self-reaction is a facile process for silyl and trimethylsilyl radicals, there remained the question: Does a first-order reaction of a silyl radical with its parent silane compete with self-reaction as a significant source of the disilane which is the major reaction product for both the silyl and trimethylsilyl radical reaction systems? As indicated in the introduction, the disappearance of silyl radicals by self-reaction does not rule out the operation of a competing first-order pathway which does not alter the silyl radical concentration. Thus chain mechanism **B** would produce disilane by a first-order process while the silyl radical concentration would decay by self-reaction. Indeed since the silyl radical concentration generated in these experiments is *ca.* $10^{-6}\ M$, in *ca.* 20 M silane solution, the first-order reaction would dominate the production of disilane if the first-order rate constant were greater than 10^{-7} times the second-order rate constant.

The relative importance of first- and second-order reactions of silyl radicals in the production of disilene, that is the chain length of mechanism **B**, can be deduced from the ratio of disilane to *tert*-butyl alcohol formed as reaction products. The chain length is equal to the reciprocal of the *tert*-butyl alcohol : disilane ratio minus one-half. For silyl and trimethylsilyl radicals ratios of *tert*-butyl alcohol to disilane of 2.6 ± 0.6 and 1.9 ± 0.4, respectively, were obtained. These product ratios imply that the chain lengths for mechanism **B** are very short, indicating that at low temperature in solution the displacement of a hydrogen atom of silane by a silyl radical is unimportant. This conclusion does not require that displacement reaction 5 also be unimportant at high temperature in the gas phase. Ring has estimated that $\log A = 10$ and $E_a = 15$ kcal/mol for reaction 5. The reaction rate extrapolated to low temperature in solution using these values is so slow that displacement could not compete with self-reaction under our reaction conditions.

The term "self-reaction" has been used in this paper and in other reports of silyl radical reaction kinetics[5] in preference to "dimerization." The latter term implies that simple coupling is the operative reaction mechanism. The present study has established that the principal self-reaction product of silyl and trimethylsilyl radicals is the dimer of the radical. However, directd imerization has *not* been established, and disproportionation is an equally plausible pathway leading to the observed principal reaction product *in the silyl radical system*.

$$2SiH_3 \longrightarrow SiH_3SiH_3 \quad \text{dimerization}$$

$$2SiH_3 \longrightarrow SiH_4 + SiH_2 \quad \text{disproportionation}$$

$$SiH_2 + SiH_4 \longrightarrow SiH_3SiH_3 \quad \text{insertion}$$

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(15) At low light intensity (9% transmission of normal light source and corresponding low radical concentration), a slight deviation from second-order disappearance of silyl radicals is observed.

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The insertion of silylene into silane is known to be efficient.[2a,23] In the silyl radical–silane system the two mechanisms dimerization and disproportionation cannot be distinguished unless a silylene scavenger is found which does not trap silyl radicals. No such reagent is known.

In the trimethylsilyl radical–trisilane system no such disproportionation mechanism can give rise to the observed product hexamethyltrisilane. Therefore it seems certain that dimerization is the mechanism for self-reaction of trimethylsilyl radicals. The small amount of *tert*-butoxytrimethylsilane formed in extended irradiations of *tert*-butyl peroxide–trimethylsilane mixtures (Figure 7) is evidently not a primary product. Its mode of formation is still being investigated.

While the argument is far from rigorous, one may point out that the similarity of rate constants and activation parameters for the self-reactions of silyl radicals and trimethylsilyl radicals makes it likely if not certain that both reactions are dimerizations in solution at low temperature.

Summary

Bimolecular self-reaction has been established as the dominant path for the disappearance of silyl and trimethylsilyl radicals dissolved in the corresponding silane. Rate constants were determined for trimethylsilyl radical self-reaction over the temperature range +20 to −82°. The activation parameters deduced from the temperature dependence of the rate constant and the rate constants themselves are typical for group IV radicals. Similar rate constants were found for the self-reaction of silyl radicals at −120 and −150°. Product studies indicate that dimerization is the principal self-reaction mechanism for trimethylsilyl radicals. A chain-carrying displacement of hydrogen atoms from a silane by a silyl or trimethylsilyl radical is not an important reaction under the present reaction conditions. The formation of disilane, the dimer of SiH_3, and the similarity of the self-reaction rates of silyl and trimethylsilyl radicals strongly suggests that direct dimerization is the mechanism for silyl radical self-reaction in solution.

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Solvation of Halide Ions in Water and Dipolar Aprotic Solvents Studied by Halogen Nucleus Nuclear Magnetic Resonance

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Abstract: Chemical shift measurements on $^{35}Cl^-$, $^{79}Br^-$, and $^{127}I^-$ in the solvents water, CH_3OH, CH_3CN, DMSO, and DMF show that the dependence on solvent is strong and that the dependence on the cations of this study, $(C_2H_5)_4N^+$, Li^+, Na^+, K^+, is comparatively weak. This suggests the use of nmr solvent shifts as a probe of the immediate environment of an ion. A close correlation between chemical shifts and the charge transfer to solvent (CTTS) uv absorption band energies strongly suggests that the nmr paramagnetic term is dominant in determining shifts, and that the important excited state is the CTTS state. The nmr behavior of Cl^- and I^- ions in mixtures of DMSO and CH_3CN with water indicated that there is no strong preference in either case for the aprotic solvent as a component of the immediate solvent environment. Rather, the strong preferential solvation which is observed in the CH_3CN–H_2O mixtures is in large part the result of the nonideal behavior of CH_3CN–H_2O mixtures. The relationship between spectroscopic studies of solvation and the thermodynamics of transfer of ions from one solvent to another is discussed.

An ion dissolved in a polar solvent has considerable influence on its surroundings. The environment of an ion may be conceptualized by a three region model. The regions are: the region of the ordering effect of the ion on its immediate neighborhood; the region of disordering of solvent structure; and the bulk region where solvent structure is unperturbed. Studies of solvation by thermodynamic or transport experiments include all effects. It has been the aim of spectroscopic studies of solvation to take advantage of the short-range interactions dominating spectroscopic observables to probe the ordering imposed by an ion on the solvent molecules directly in contact with it.

Solvent dependent nmr shifts of the nuclei ^{59}Co, ^{23}Na, and ^{35}Cl have been proposed as measures of the composition of the immediate solvation shell[2-4] with the suggestion that shifts should vary approximately

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