the effect appears to be a general phenomenon which complements mass spectrometry in ^{18}O-labeling studies.[15] We are currently investigating the influence of hybridization changes on shift magnitude and applications in secondary metabolism.

Acknowledgments. The author is grateful to Dr. T. Nakashima and Mr. G. Bigam for spectral measurements and useful discussions. This investigation was supported by University of Alberta General Research Fund Grant 55-32837 and Natural Sciences and Engineering Research Council of Canada (NSERC) Grant A0845. Initial measurements in December 1977 at Stanford Magnetic Resonance Laboratory were supported by NSF GP 23633 and NIH RR00711.

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(5) Our first experiments were done with pulegone using Stanford Magnetic Resonance Laboratory's HXS-360 at 90 MHz. We are grateful to Drs. W. Conover and G. Sullivan for making these measurements.

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Received August 27, 1979

Disproportionation of Trimethylsilyl at 25 °C. Mercury Photosensitization of Trimethylsilane

Sir:

While the disproportionation of trimethylsilyl radicals has been invoked under pyrolysis conditions,[1] this reaction has been suggested on a number of occasions to be negligible at or near room temperature.[2-6] Nay, Woodall, Strausz, and Gunning have examined the mercury photosensitization of trimethylsilane with some care.[6] This method was also used by Cadman, Tilsley, and Trotman-Dickenson to generate $(CH_3)_3Si$ for a gas-phase rotating-sector experiment.[3] Both groups indicated they did not expect reaction 1 to be important and found no evidence to contradict that expectation. Recent developments suggest a reexamination of this system may be justified.

$$2(CH_3)_3Si \rightarrow (CH_3)_3SiH + [(CH_3)_2SiCH_2] \qquad (1)$$

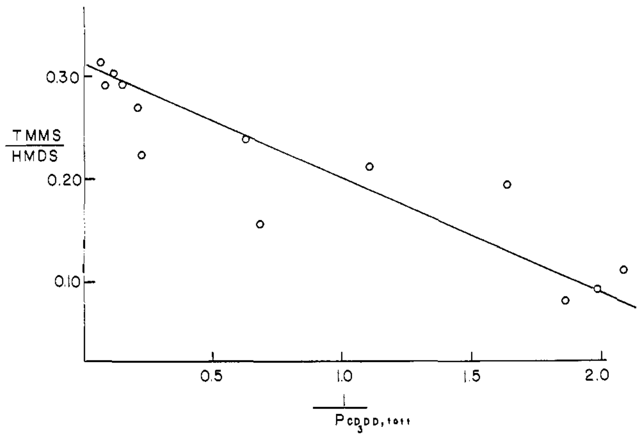

Figure 1. Ratio of the quantum yield of trimethylmethoxysilane to hexamethyldisilane plotted vs. reciprocal methanol-d_4 pressure (in Torr). Least-squares fit intercept is 0.31 ± 0.08.

$[(CH_3)_2SiCH_2]$ produced in the gas phase by pyrolysis dimerizes to 1,1,3,3-tetramethyl-1,3-disilacyclobutane in good yield.[7] The dimer, however, apparently does not form near room temperature when $[(CH_3)_2SiCH_2]$ is produced by gas-phase photolysis.[8] Since the other product of reaction 1 is the starting material, $(CH_3)_3SiH$, this reaction could easily go unnoticed while still occurring.

In a recent discussion of the photolysis of tetramethylsilane,[9] we reported a ratio of the rate of reaction 1 to reaction 2 of 0.48 ± 0.2. The large uncertainty in our value for k_1/k_2, the ready availability of trimethylsilyl radicals from Hg photosensitization of trimethylsilane, and the possibility that reaction 1 was overlooked in earlier work all suggest that this system be reexamined with emphasis on possible detection of $[(CH_3)_2SiCH_2]$.

$$2(CH_3)_3Si \rightarrow (CH_3)_6Si_2 \qquad (2)$$

Small amounts of methanol have been demonstrated to be an effective, though not quantitative, trap for $[(CH_3)_2SiCH_2]$ in the gas phase.[8] Trimethylsilane, 120 Torr, and 0.6 to 12 Torr of perdeuterated methanol in a quartz vessel fitted with a Teflon stopcock (Kontes) and containing a small droplet of Hg were placed in a Rayonet photochemical reactor fitted with low pressure mercury lamps. Products were analyzed as reported previously using a gas chromatograph and mass spectrometer.[8]

Trimethylmethoxysilane, the expected addition product of $[(CH_3)_2SiCH_2]$ and CH_3OH, is found in good yield in these experiments. Figure 1 plots the ratio of $(CH_3)_2CH_2DSiOCD_3/(CH_3)_6Si_2$ vs. $[CD_3OD]^{-1}$. The intercept of this plot is presumed to correspond to the limiting yield of $(CH_3)_2CH_2DSiOCD_3$ and this is a direct measure of k_1/k_2. This value is 0.31 ± 0.08. Since the quenching cross section[6] for Me_3SiH is about three times larger than that for methanol,[10] and since $P(Me_3SiH)/P(CD_3OD) \geq 10$, it seems highly unlikely that $(CH_3)_2CH_2DSiOCD_3$ arose owing to sensitization of the methanol. The incorporation of all of the methanol-d_4 deuterium into the trimethylmethoxysilane is also consistent with its production as an addition of methanol-d_4 to $[(CH_3)_2SiCH_2]$. In their earlier work, Nay et. al. found the limiting quantum yield of $(CH_3)_6Si_2$ to be 0.78 while products of less methylated silanes corresponded to a unit quantum yield. If the difference between $\Phi[(CH_3)_6Si_2]$ and unity is ascribed to reaction 1, then $k_1/k_2 = 0.28$, a value similar to that determined in this work.

It appears to us that disproportionation of $(CH_3)_3Si$ is a self-reaction competitive with combination of these radicals. Failure to discern it in earlier work[2-6] most likely is the result

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of the failure of $[(CH_3)_2SiCH_2]$ to give readily identifiable products in the absence of a specific trap.

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Disproportionation of Trimethylsilyl Radicals to a Sila Olefin in the Liquid Phase

Sir:

Until very recently the disproportionation of trimethylsilyl radicals to the sila olefin 2-methyl-2-silapropene was considered to be a minor process compared to radical recombination.[1]

$$\begin{tikzcd}
 & \mathrm{Me_3SiH + CH_2{=}SiMe_2} \\
\mathrm{2Me_3Si\cdot} \arrow[ur, "k_{\mathrm{disp}}"] \arrow[dr, "k_{\mathrm{recomb}}"'] & \\
 & \mathrm{Me_3SiSiMe_3}
\end{tikzcd}$$

We have reexamined the self-reactions of trimethylsilyl radicals in solution, prompted by the high ratio of disproportionation to recombination, $k_{\mathrm{disp}}/k_{\mathrm{recomb}} = 0.48$, found in the gas phase by Tokach and Koob.[2] We find that disproportionation is also an important process for trimethylsilyl radicals in the liquid phase.

When trimethylsilyl radicals are generated by photolysis of *tert*-butyl peroxide in solutions of trimethylsilane,[3] the disappearance of $Me_3Si\cdot$ as monitored by kinetic ESR spectroscopy is a rapid process, second order in the concentration of $Me_3Si\cdot$.[4,5]

$$Me_3COOCMe_3 + h\nu \rightarrow 2Me_3CO\cdot$$

$$Me_3CO\cdot + Me_3SiH \rightarrow Me_3COH + Me_3Si\cdot$$

$$2Me_3Si\cdot \rightarrow \text{products}$$

Based on the observation of hexamethyldisilane and *tert*-butyl alcohol as the sole reaction products at the short reaction times of the kinetic studies, radical recombination was believed to be the exclusive mode of self-reaction for trimethylsilyl radicals.[5] A third product found at longer irradiation times, *tert*-butoxytrimethylsilane, $Me_3COSiMe_3$, was believed to be a secondary product,[5] but we now know that it is formed by trapping of the disproportionation product by *tert*-butyl alcohol.[6]

$$Me_3COH + CH_2{=}SiMe_2 \rightarrow Me_3COSiMe_3$$

In the kinetic studies *tert*-butyl alcohol is generated in situ, and thus initially there is no trapping reagent present capable of converting the sila olefin into a stable low molecular weight product.[7] We have now established that *tert*-butoxytrimethylsilane is an early product when trapping reagent is present and is formed from addition of alcohol to sila olefin. Several alternative mechanisms for formation of $Me_3COSiMe_3$ have been eliminated.

In the presence of excess *tert*-butyl alcohol, the product ratio of $Me_3COSiMe_3/Me_3SiSiMe_3 = 0.19 \pm 0.05$ remained constant with irradiation time. That 2-methyl-2-silapropene was being trapped was demonstrated by use of Me_3COD either generated in situ from Me_3SiD or added in excess.

$$Me_3COD + CH_2{=}SiMe_2 \rightarrow Me_3COSiMe_2CH_2D$$

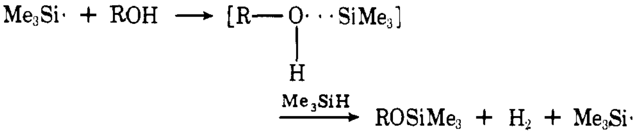
Formation of this monodeuterated *tert*-butoxytrimethylsilane was established by ^{1}H NMR and mass spectroscopy. There is a scatter in the quantitative results covering a range of incorporation from 0.3 to 0.8 deuterons/molecule.[8,13] Thus the labeling experiments do not exclude contributions from additional sources of *tert*-butoxytrimethylsilane. Three such sources have been considered. (1) Attack by *tert*-butoxy radicals on hexamethyldisilane

$$Me_3CO\cdot + Me_3SiSiMe_3 \rightarrow Me_3COSiMe_3 + Me_3Si\cdot$$

has been rendered unlikely by the absence of either product when *tert*-butoxy radicals were generated in hexamethyldisilane.[5] (2) Induced decomposition of *tert*-butyl peroxide

$$Me_3Si\cdot + Me_3COOCMe_3 \rightarrow Me_3COSiMe_3 + Me_3CO\cdot$$

can also be ruled out as a source of *tert*-butoxytrimethylsilane, since the presence of *tert*-butyl alcohol is required for its formation. Irradiation of mixtures of *tert*-butyl peroxide, trimethylsilane, and *methanol* yields *methoxytrimethylsilane* and hexamethyldisilane as products, with only traces of *tert*-butoxytrimethylsilane.[9] Thus the alkoxysilane arises from reaction of a silicon-containing intermediate with an alcohol. (3) A remaining possibility was that it is the trimethylsilyl radical itself that reacts with an alcohol molecule to form an alkoxysilane via an unconventional radical complex that could act as a hydrogen atom donor in a chain process:[10]



$$Me_3Si\cdot + ROH \longrightarrow [R{-}\underset{\displaystyle H}{\underset{|}{O}}\cdot\cdot\cdot SiMe_3] \xrightarrow{Me_3SiH} ROSiMe_3 + H_2 + Me_3Si\cdot$$

A very low yield (<2%) of hydrogen speaks against this interesting process.

Since positive evidence for the formation of $CH_2{=}SiMe_2$ is given by the trapping experiments with deuterated *tert*-butyl alcohol, we believe that the disproportionation of trimethylsilyl radicals in solution is established. The observed product ratio of $Me_3COSiMe_3/Me_3SiSiMe_3 = 0.2$ is insensitive to variation of alcohol concentrations above 10 mol % and thus may be equated with the ratio of bimolecular rate constants for disproportionation and recombination of trimethylsilyl radicals. Since the recombination rate is nearly at the diffusion-controlled limit,[5] the disproportionation is astonishingly rapid,[11] perhaps owing to stabilization of the transition state by the incipient carbon-silicon π bond. Facile disproportionation of trimethylsilyl radicals may therefore be taken as indirect evidence for substantial π bonding in the sila olefin.

0002-7863/80/1502-0377$01.00/0