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.

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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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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.

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

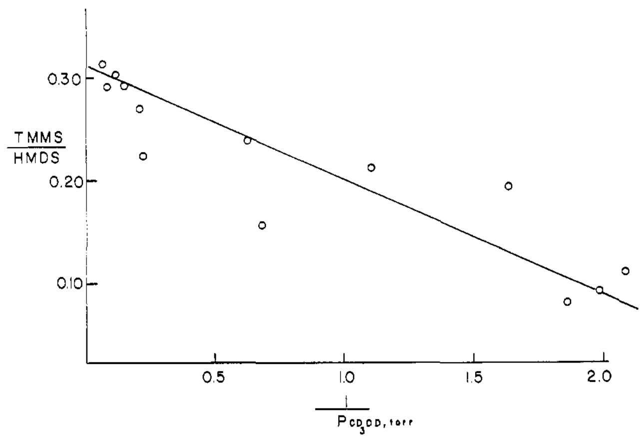

Figure 1. Ratio of the quantum yield of trimethylmethoxysilane to hexamethyldisilane plotted vs. reciprocal methanol-d_4 pressure (in Torr). Least-squares fit intercept is 0.31 ± 0.08.

$[(CH_3)_2SiCH_2]$ 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 $P(Me_3SiH)/P(CD_3OD) \geqslant 10$, 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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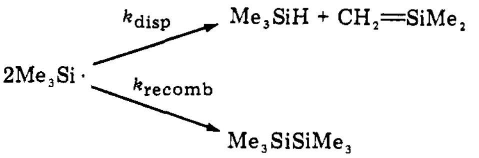
Disproportionation of Trimethylsilyl Radicals to a Sila Olefin in the Liquid Phase

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]



We have reexamined the self-reactions of trimethylsilyl radicals in solution, prompted by the high ratio of disproportionation to recombination, $k_{disp}/k_{recomb} = 0.48$, 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.

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

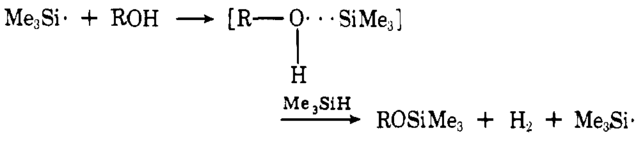
Formation of this monodeuterated *tert*-butoxytrimethylsilane was established by ^1H NMR and mass spectroscopy. There is a scatter in the quantitative results covering a range of incorporation from 0.3 to 0.8 deuterons/molecule.[8,13] Thus the labeling experiments do not exclude contributions from additional 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.

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