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

References and Notes

(1) Clifford, R. P.; Gowenlock, R. G.; Johnson, C. A. F.; Stevenson, J. *J. Organomet. Chem.* **1972,** *34,* 53. Later work (Baldwin, A. C.; Davidson, I. M. T.; Reed, M. D. *J. Chem. Soc., Faraday Trans 1* **1978,** *74,* 2171) invokes H abstraction from parent by $(CH_3)_3Si$ to account for observed $(CH_3)_3SiH$ rather than the disproportionation reaction proposed by Clifford et al. The matter of the role of disproportionation of $(CH_3)_3Si$ at elevated temperatures cannot be considered settled.

(2) Cadman, P.; Tilsley, G.; Trotman-Dickenson, A. F., presented at Gas Kinetics and Photochemistry Meeting, University College, Cardiff, 1970, cited in ref 1.

(3) Cadman, P.; Tilsley, G. M.; Trotman-Dickenson, A. F. *J. Chem. Soc., Faraday Trans. 1* **1972,** *68,* 1849.

(4) Gaspar, P. P.; Haizlip, A. D.; Choo, K. Y. *J. Am. Chem. Soc.* **1972,** *94,* 9032. Gaspar has reexamined this system in light of the results of ref 9 and has reported in a communication to us that a value of $k_1/k_2 = 0.2$ is consistent with his new findings.

(5) Strausz, O. P.; Gammie, L.; Theodorakoupoulos, G.; Mezey, P. G.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1976,** *98,* 1622.

(6) Nay, N. A.; Woodall, G. N. C.; Strausz, O. P.; Gunning, H. G. *J. Am. Chem. Soc.* **1965,** *87,* 179.

(7) Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968,** *419,* 1396.

(8) Tokach, S. K.; Boudjouk, P.; Koob, R. D. *J. Phys. Chem.* **1978,** *82,* 1203, and references therein.

(9) Tokach, S. K.; Koob, R. D. *J. Phys. Chem.* **1979,** *83,* 700.

(10) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.

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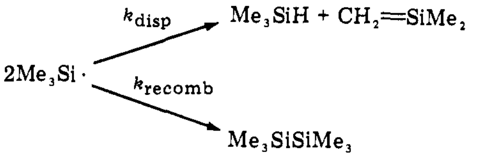
Disproportionation of Trimethylsilyl Radicals to a Sila Olefin in the Liquid Phase

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 $Me_3Si·$ as monitored by kinetic ESR spectroscopy is a rapid process, second order in the concentration of $Me_3Si·$.[4,5]

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

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

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

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.

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

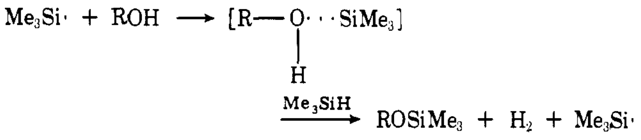
Formation of this monodeuterated *tert*-butoxytrimethylsilane was established by ^1H NMR and mass spectroscopy. There is a scatter in the quantitative results covering a range of incorporation from 0.3 to 0.8 deuterons/molecule.[8,13] Thus the labeling experiments do not exclude contributions from additional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

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

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

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

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]



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

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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$$Me_3Si\cdot + HCH_2\dot{S}iMe_2 \rightarrow [Me_3Si \cdots H \cdots CH_2 \overset{\cdots}{=} SiMe_2]^{\ddagger} \rightarrow Me_3SiH + CH_2{=}SiMe_2$$

A final point of interest is an increase at long irradiation times (>12 h) of the yield of $Me_3COSiMe_3$ and a concomitant decrease in the yield of $Me_3SiSiMe_3$. Trapping experiments with labeled alcohol indicate that photolysis of hexamethyldisilane is another route to 2-methyl-2-silapropene. This has also been observed by Boudjouk and Koob in the gas phase.[12]

$$Me_3SiSiMe_3 + h\nu \rightarrow Me_3SiH + CH_2{=}SiMe_2$$

Acknowledgments. We thank Professor Thomas J. Barton for stimulating discussions of this problem and for helpful suggestions; we also thank Mr. Daniel Graham for mass spectrometric analyses. Financial support from the Department of Energy is gratefully acknowledged. This is technical report C00-1718-78.

References and Notes

(1) A ratio of k_{disp}/d_{recomb} = 0.046 has been quoted without experimental details: O. P. Strausz, L. Gammie, G. Theodorakoupolos, P. G. Mezey, and I. G. Csimadia, *J. Am. Chem. Soc.*, **98,** 1624 (1976).

(2) S. K. Tokach and R. D. Koob, *J. Phys. Chem.*, **83,** 774 (1979); see also S. K. Tokach and R. D. Koob, *J. Phys. Chem.*, **83,** 774 (1979); see also S. K. Tokach and R. D. Koob, "Trimethylsilyl Radical: H-Abstraction and Disproportionation Reactions", abstract, XIII Organosilicon Symposium, University of Michigan, March 30–31, 1979.

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

(4) P. T. Frangopol and K. U. Ingold, *J. Organomet. Chem.*, **25,** C9 (1970); C. B. Watts and K. U. Ingold, *J. Am. Chem. Soc.*, **94,** 491 (1972).

(5) P. P. Gaspar, A. D. Haizlip, and K. Y. Choo, *J. Am. Chem. Soc.*, **94,** 491 (1972).

(6) Addition of alcohols to sila olefins is now a well-known reaction: L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8,** 18 (1975).

(7) In the gas phase no low molecular weight products have been found from $CH_2{=}SiMe_2$ at room temperature in the absence of trapping reagent: S. Tokach, P. Boudjouk, and R. D. Koob, *J. Phys. Chem.*, **82,** 1204 (1978). At high temperatures dimers are formed; see ref 6.

(8) These are strictly lower limits. The mass spectrometric deuterium assay of *tert*-butoxytrimethylsilane will be discussed in a full report of this work.

(9) Control experiments showed that exchange of alkoxy groups did not occur for the product methoxytrimethylsilane nor for the recovered *tert*-butyl peroxide.

(10) This mechanistic possibility was suggested by the observation of ESR spectra by J. F. S. Wan and K. Y. Choo indicative of addition of silyl radicals to siloxanes: private communication from Professor Wan.

(11) It has been pointed out[1] that hydrogen atom abstraction from $Me_3Si\cdot$ must be $>10^5$ as rapid as abstraction from Me_4Si for disproportionation of trimethylsilyl radicals to be competitive with radical recombination.

(12) P. Boudjouk and R. D. Koob, "On the Photolysis of Disilanes as a Source of Silaethylenes", abstract, XIII Organosilicon Symposium, University of Michigan, March 30–31, 1979. These workers employed 148-nm radiation, while in our experiments unfiltered low- and medium-pressure mercury lamps are used. Our findings were also presented in an abstract to this symposium: P. P. Gaspar and B. J. Cornett, "Disproportionation of Silyl Radicals to Silenes in the Liquid Phase".

(13) NOTE ADDED IN PROOF. A photochemical reaction between alcohols and trimethylsilane contributes to the yield of alkoxytrimethylsilane, but does *not* lead to incorporation of deuterium from the hydroxyl group into the product.

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Disproportionation and Hydrogen Abstraction Reactions of Trimethylsilyl Radicals

Sir:

Information on the disproportionation and metathetical reactions of silyl radicals is sparse. Early studies from this laboratory[1] on the monomethyl-, dimethyl-, and trimethylsilyl radicals have already indicated that disproportionation of these radicals may occur parallel to combination. Unambiguous evidence for the disproportionation reactions of the SiH_3SiH_2 and SiH_3 radicals was reported in 1973.[2] Disilyl radicals were shown to undergo pressure dependent disproportionation up to at least 400 Torr of Si_2H_6 pressure, where $k_d/k_c = 0.1$. The SiH_3 radicals were shown to disproportionate nearly completely at room temperature and at a few Torr of SiH_4 plus up to 800 Torr of H_2, as determined from the isotopic distribution of the disilane products from the H + SiH_4/SiD_4 reaction giving relative concentrations for Si_2D_6, Si_2H_6, and SiH_3SiD_3 of 9.7, 57.2, and 0.3, respectively, from an equimolar mixture of SiH_4 and SiD_4. Subsequently, Potzinger et al.[3] reported a k_d/k_c value of 0.7 for SiH_3 radicals at infinite pressure. In 1976 a k_d/k_c value of 0.05 was reported[4] for trimethylsilyl radicals from the photolysis of $(CH_3)_3SiHgSi(CH_3)_3$.

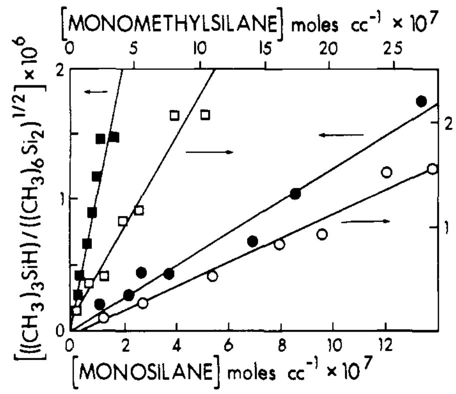

Figure 1. Relative rate plots for the abstraction-combination reactions of trimethylsilyl radicals with added monosilane (■), monosilane-d_4 (●), monomethylsilane (□), and monomethylsilane-d_3 (○).

In more recent developments Tokach and Koob used alcohol scavenging techniques for trapping trimethylsilyl radicals[5] and found a k_d/k_c value of 0.31.[6] Gaspar et al.,[7] using the same technique in the liquid phase, obtained $k_d/k_c = 0.19$.

We now report evidence for the cross disproportionation of trimethylsilyl radicals and approximate values for k_d/k_c along with rate constant data for the hydrogen abstraction reactions of trimethylsilyl radicals with a series of silicon hydrides and isobutane.

Trimethylsilyl radicals were generated by the room temperature photolysis of bis(trimethylsilyl)mercury vapor (~0.1 Torr) using the Pyrex-filtered radiation of a medium-pressure mercury lamp. The three retrievable products were hexamethyldisilane (HMDS), trimethylsilane, and hexamethyldisiloxane (HMDSO) in relative yields of 84:4:12. Scavenging experiments using either NO, O_2, or C_2H_4 indicated that HMDS and Me_3SiH formation can be suppressed and consequently these products arise via the combination and disproportionation reactions of trimethylsilyl radicals. The yield of HMDSO cannot be suppressed by scavengers and this product seems to result from a dark reaction between the source compound and the wall of the reaction vessel. From these results the following sequence of elementary steps can be deduced for the photolysis of bis(trimethylsilyl)mercury:

$$[(CH_3)_3Si]_2Hg + h\nu\ (\lambda \geq 300\ \text{nm}) \rightarrow 2(CH_3)_3Si + Hg \tag{1}$$

$$2(CH_3)_3Si \rightarrow HMDS \tag{2}$$

$$2(CH_3)_3Si \rightarrow (CH_3)_3SiH + (CH_3)_2SiCH_2 \tag{3}$$

$$[(CH_3)_3Si]_2Hg \xrightarrow{\text{wall}} HMDSO + Hg \tag{4}$$

Auxiliary studies have shown that the displacement reaction

$$(CH_3)_3Si + [(CH_3)_3Si]_2Hg \rightarrow (CH_3)_6Si_2 + Hg + (CH_3)_3Si \tag{5}$$

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