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

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]

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

References and Notes

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(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
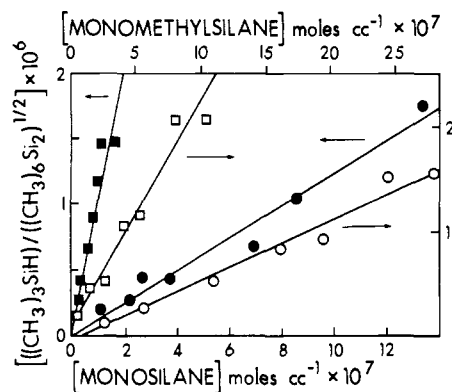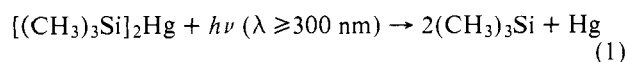

Figure 1. Relative rate plots for the abstraction–combination reactions of trimethylsilyl radicals with added monosilane (■), monosilane-d_4 (●), monomethylsilane (□), and monomethylsilane-d_3 (○).

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 $(CH_3)_3SiHgSi(CH_3)_3$.

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:

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

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

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

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

Auxiliary studies have shown that the displacement reaction

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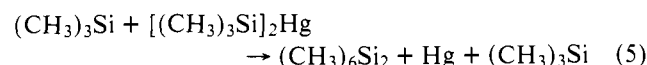$$\rightarrow (CH_3)_6Si_2 + Hg + (CH_3)_3Si \tag{5}$$

Table I. Relative Rate Constants for Reaction of Trimethylsilyl Radicals with Nondeuterated and Deuterated Silanes

reaction	$k_{abstr}/k^{1/2}_{comb}$	k_{abstr},[a,b] cm^3 mol^{-1} s^{-1}	isotope effect	$k_{abstr}^{CH_3}$,[c] cm^3 mol^{-1} s^{-1}	isotope effect
$(CH_3)_3Si + Si_2H_6$	$(5.25 \pm 0.82) \times 10^2$	3.25×10^8	5.8	6.9×10^7	5.7
$(CH_3)_3Si + Si_2D_6$	$(8.91 \pm 1.47) \times 10$	5.57×10^7		1.2×10^7	
$(CH_3)_3Si + SiH_4$	7.61 ± 1.2	6.51×10^6	7.0	5.0×10^6	5.3
$(CH_3)_3Si + SiD_4$	$(9.86 \pm 0.78) \times 10^{-1}$	9.32×10^5		9.5×10^5	
$(CH_3)_3Si + MeSiH_3$	1.64 ± 0.18	1.95×10^6	3.4	2.1×10^6	6.8
$(CH_3)_3Si + MeSiD_3$	$(4.73 \pm 0.36) \times 10^{-1}$	5.72×10^5		3.1×10^5	
$(CH_3)_3Si + Me_2SiH_2$	$(4.33 \pm 0.57) \times 10^{-1}$	4.73×10^5	1.8	1.0×10^6	3.6
$(CH_3)_3Si + Me_2SiD_2$	$(2.58 \pm 0.12) \times 10^{-1}$	2.55×10^5		2.8×10^5	
$(CH_3)_3Si + (CH_3)_3CH$	$(4.15 \pm 0.74) \times 10^{-2}$	2.55×10^4		5.1×10^5	

[a] Calculated with the value $k_{comb} = 1.5 \times 10^{12}$ cm^3 mol^{-1} s^{-1}. [b] Corrected for cross disproportionation. [c] References 13 and 14.

Table II. Values of k_d/k_c for Various Silyl and Methylated Silyl Radicals

reaction	k_d/k_c (25 °C)
$(CH_3)_3Si + (CH_3)_3Si \rightarrow (CH_3)_3SiH + CH_2{=}Si(CH_3)_2$	0.05,[a] 0.03,[b] 0.31,[c] 0.19[d]
$(CH_3)_3Si + (CH_3)_2SiH \rightarrow (CH_3)_3SiH + CH_2{=}SiHCH_3 + (CH_3)_2Si$	0.3[a]
$(CH_3)_3Si + (CH_3)SiH_2 \rightarrow (CH_3)_3SiH + CH_2{=}SiH_2 + CH_3SiH$	0.5[a]
$(CH_3)_3Si + SiH_3 \rightarrow (CH_3)_3SiH + SiH_2$	0.8[a]
$(CH_3)_2SiH + (CH_3)_2SiH \rightarrow (CH_3)_2SiH_2 + CH_2{=}SiHCH_3$	0.1[b]
$CH_3SiH_2 + CH_3SiH_2 \rightarrow CH_3SiH_3 + CH_2{=}SiH_2$	0.1[b]
$CH_3SiD_2 + CH_3SiD_2 \rightarrow CH_3SiD_2H + CH_2{=}SiD_2$	0.04[b]
$Si_2H_5 + Si_2H_5 \rightarrow Si_2H_6 + SiH_2{=}SiH_2$	0.1 at 400 Torr, pressure dependent[2]
$SiH_3 + SiH_3 \rightarrow SiH_4 + SiH_2$	0.7^2 at ∞ pressure, pressure dependent[3]

[a] Present work. [b] Reference 1. [c] Reference 6. [d] Reference 7.

is of very minor importance and can be neglected.

The ratio of Me₃SiH to HMDS, which is equal to k_d/k_c, has a value of 0.05 ± 0.01 as determined from 12 experiments and is independent of added N₂ pressure up to 200 Torr.

When the photolysis of the source molecule was carried out in the presence of one of the hydrogen donors (HSiR₃) listed in Table I, the yield of Me₃SiH increased and the yield of HMDS decreased according to the kinetic relation

$$R(Me_3SiH)/R(HMDS)^{1/2} = (k_{abs}/k_c^{1/2})[HSiR_3] \quad (I)$$

derived from the simple steady-state treatment of the competing reactions 2, 3, and

$$(CH_3)_3Si + HSiR_3 \rightarrow Me_3SiH + SiR_3 \quad (6)$$

When the ratio (Me₃SiH)/(HMDS)$^{1/2}$ was plotted as a function of the substrate pressure, a good linear relationship was obtained. Some illustrative examples are given in Figure 1. Least-squares treatment of the plots gave the relative rate constants listed in Table I for the abstraction reactions. First-order plots of the results did not yield straight lines but instead curves were obtained, supporting the assumption that HMDS is formed by the combination of trimethylsilyl radicals.

The relative rate constants for abstraction by trimethylsilyl radicals are calculated on the assumption that abstraction from HSiR₃ is the sole source of Me₃SiH. However, the possibility of other sources of Me₃SiH should be carefully considered. The formation of Me₃SiH from the self-disproportionation of the trimethylsilyl radicals can be accounted for by using the experimentally obtained ratio for k_d/k_c. The most likely additional source is the cross disproportionation between a trimethylsilyl radical and the SiR₃ radical formed in the abstraction step 6.

The amount of Me₃SiH formed by cross disproportionation could be calculated from the measurement of the cross combination product using the following relationship:

$$[(CH_3)_3SiH]_{cr\text{-}disp} = \frac{1}{2}\{[(CH_3)_3SiH]_{total}$$
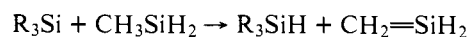$$- (CH_3)_3SiSiR_3\} \quad (II)$$

From the amount of the cross-combination products measured for each silane over the pressure range studied, the cross-disproportionation–combination rate constant ratios for the various SiR₃ radicals with the trimethylsilyl radical were calculated and the results are given in Table II. k_d/k_c values calculated from earlier work in this laboratory on the Hg-photosensitized decomposition of silanes are also given in the same table.

The experimental rate constants for the combination of trimethylsilyl radicals available in the literature[8-10] are in the range of (1.2–2.75) × 10¹² cm³ mol⁻¹ s⁻¹. We used[11] a value of 1.5 × 10¹² cm³ mol⁻¹ s⁻¹ for the calculation of absolute rates of abstraction from the measured relative rate constants. The results are given in Table I, together with the rate constants for H abstraction by CH₃ radicals for comparison. The calculated rate constants for the trimethylsilyl radical are surprisingly high but are in agreement with the observed high abstractive ability of this radical as reported by Tokach and Koob[5] and Gammie et al.[12] and appear to reflect a diminished triplet repulsion in the ⟩Si· ·H· ·Si⟨ as compared with the ⟩C· ·H· ·Si⟨ activated complex.

Comparing the three different values, 0.31 (Tokach and Koob[6]), 0.19 (Gaspar et al.[7]), and 0.05 (present work) for k_d/k_c of trimethylsilyl radicals, it is seen that the scatter is substantial, but there is no disagreement with respect to the occurrence of the disproportionation of trimethylsilyl radicals.

From the ratio $k_d/k_c = 0.05$ and from $k_c = 1.5 \times 10^{12}$ cm³ mol⁻¹ s⁻¹ the rate constant for the disproportionation equal to 7.5 × 10¹⁰ cm³ mol⁻¹ s⁻¹ is more than six orders of magnitude higher than the rate constant for the H abstraction from (CH₃)₃CH manifesting the importance of the assistance arising from the C–Si double bond formation to the overall energetics of the disproportionation reaction.

With Si₂H₅ and radicals containing Si–H and Si–C bonds, two types of disproportionation reactions are feasible: one yielding silaethylene,

$$R_3Si + CH_3SiH_2 \rightarrow R_3SiH + CH_2{=}SiH_2$$

and the other, silylene,

$$R_3Si + CH_3SiH_2 \rightarrow R_3SiH + CH_3SiH$$
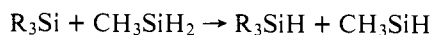
The data in Table II for self-disproportionation refer to the silaethylene-yielding reactions, and those for cross disproportionation, to the sum of the silaethylene- and silylene-producing reactions.[15]

Thus, we conclude that disproportionations of silyl radicals are of general occurrence and further detailed studies are warranted.

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(15) The terms self- and cross disproportionation refer to the reactions of two identical and two different radicals.

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Chemical Geometrodynamics: Gravitational Fields Can Influence the Course of Prochiral Chemical Reactions

Sir:

The following discussion will show that, in principle, the dynamics of geometry in prochiral chemical reactions can be controlled by the macroscopic geometry of chiral physical fields in which the reactions proceed. Prochiral chemical reactions are capable of producing chiral products; however, without dissymmetric catalysts, solvents or physical fields, or extremely unusual statistics, the reactions would produce only racemic products.

The question of the potential effect of parallel (chiral) combinations of electric, **E**, and magnetic, **B**, fields on prochiral chemical reactions has been the subject of three recent re-

ports.[1-3] We originally asserted that it would be possible to obtain asymmetric synthesis using chiral **E** and **B** fields, if the prochiral reactant had an intrinsic magnetic moment, and if it were possible to select one of the two magnetic species [A (j) or A (−j)].[3] It appears from the theorem by deGennes[1] that

A
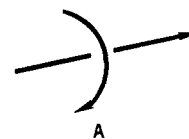
it would be impossible to select one of the magnetic species using only **E** and **B** fields. Thus, for electric and magnetic fields, asymmetric synthesis must depend on nonadiabatic currents in the transition state.[3] A realistic estimate of the magnitude of possible nonadiabatic currents and their contribution to asymmetric synthesis suggests that an enantiomeric excess of 1 ppb is all that one could expect with readily attainable fields.[4]

The three other physical fields that could be considered for use in field-directed, asymmetric synthesis are strong, weak, and gravitational. Both strong and weak fields have ranges much less than molecular diameters; so neither of these fields could contribute to a chiral macroscopic field structure. The remaining field is gravitational.[5] In the following paragraphs we will show that, in principle, it is possible to direct an asymmetric synthesis with a chiral physical field, the polar component of which is gravitational.

In constructing a chiral field containing a gravitational component the gravitational field can be either continuous or quantal (gravitons or gravitational phonons). In the former case a chiral gravitational field can be represented by the vector diagram A in which the polar vector represents linear acceleration and the axial vector represents centrifugal motion. Molecules moving under the influence of this field structure would have both linear momentum, p, and angular momentum, σ. Parity, P, and time reversal, T, operators are used to illustrate the possibility of asymmetric synthesis in this chiral field. The arguments are directly analogous to the case of the electromagnetic field.[1-3]

Given a molecule, M, moving in a chiral gravitational field such that it has a linear momentum, p, and angular momentum, σ, application of the parity operator, P, to this system will give the enantiomeric molecule, M*, with enantiomeric momenta:

$$(M, p, \sigma) \ P \ (M*, -p, \sigma) \ T \ (M*, p, -\sigma) \qquad (1)$$

Application of the time reversal operator T will leave both the molecule and the chirality of the momenta unchanged (1). It is well known that collision velocities can influence the rates of chemical reactions. Thus it appears that a chiral gravitational field which will impart chiral momenta to reacting species could cause asymmetric synthesis.

It is possible to construct a macroscopic analogue for the change in the energy of a chiral transition state caused by a chiral field. Imagine a right- and a left-handed propeller in separate wind tunnels, designed to produce the chiral field in A by gas motion. The right-handed propeller would rotate at a higher rate than the left-handed one.

Consideration of a chiral field in which the gravitational component is quantal, **G**, is entirely analogous. In this case the axial vector field might be magnetic, **B**. Application of the parity operator to the molecule, M, and chiral field will give the enantiomeric molecule M* and the enantiomeric field (2). Neither the molecule nor the field structure will be altered by the time reversal (2), a situation which is compatible with asymmetric synthesis.[6] Gravitational phonons should influence molecular translation.