naphthalene-like emission remains approximately constant with increasing cyclodextrin concentration. The observation of two lifetimes is probably due to two complexes of different geometry. The exciplex lifetimes are 5, 7, and 11 ns for ethanol, acetonitrile, and β-cyclodextrin solutions, respectively (Table I).

The data support a model where **1** forms an emissive 1:1 complex with β-cyclodextrin in water. Surprisingly, the β-cyclodextrin cavity for exciplex has a polarity similar to that of ethanol, considerably higher than anticipated. The results suggest that the intramolecular exciplex of **1** formed must be situated near the top of the β-cyclodextrin cavity in the proximity of OH groups, an environment considerably different from that of excimers. Exciplexes, which possess intrinsic charge-transfer character, are more polar than excimers. Their formation is governed by a delicate balance between their stabilization and dissociation to ion pairs by the polar environment.

The failure to observe intramolecular exciplex emission of **1** in α-cyclodextrin and in γ-cyclodextrin may be attributed to steric factors. The former possesses too small a cavity for association with **1**, while the latter possesses too large a cavity, where polar water molecules may enter freely to cause the dissociation of the exciplex to ion pairs. The effect of cyclodextrins on other intramolecular exciplex systems is being investigated.

**Acknowledgment.** G.S.C. and N.J.T. thank the Army Office of Research and N.Y. and M.-J.C. thank the National Science Foundation for their generous support of this research.

**Registry No. 1**, 25913-62-6; β-cyclodextrin, 7585-39-9; α-cyclodextrin, 10016-20-3; γ-cyclodextrin, 17465-86-0.

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## Formation of Thermalized Singlet Silylene in the Reactions of Recoiling Silicon Atoms[†]

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*Received May 11, 1983*

The 1966 suggestion that silylene ($SiH_2$) is formed in the gas-phase reactions of high-energy recoiling silicon atoms[1] has been successful in accounting qualitatively for many of the chemically stable end products detected in these "hot atom" experiments.[1-7] Since studies of thermally generated silylene had led to an estimate of 1.2 for the relative reactivity of silane and butadiene toward *singlet silylene* at 385 °C, it was disconcerting to find that silane was 9 times as reactive as butadiene toward a common intermediate, X, formed from recoiling silicon atoms in ternary mixtures of phosphine,[8] silane, and butadiene.[9]

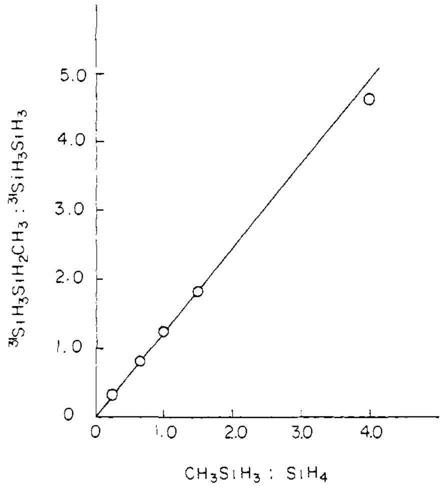
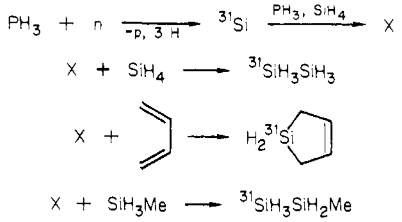


**Figure 1.** Ratio of disilane products $^{31}SiH_3SiH_2CH_3$:$^{31}SiH_3SiH_3$ as a function of substrate ratio $CH_3SiH_3$:$SiH_4$ in the reactions of recoiling $^{31}Si$ atoms in mixtures of 500 torr $PH_3$ and 500 torr $CH_3SiH_3$ + $SiH_4$.

Scheme I



Scheme I includes the reaction of X with methylsilane, since competition experiments have now been undertaken with ternary mixtures of phosphine, silane, and methylsilane to answer the question: is X really ground-state singlet silylene? The $SiH_3Me$, $SiH_4$ substrate pair was chosen for recoil experiments because its relative reactivity toward thermally generated $SiH_2$ had been measured.[10]

When the yield ratios of $^{31}SiH_3SiH_2Me$ and $^{31}SiH_3SiH_3$, the products expected from Si–H insertion by nucleogenic $^{31}SiH_2$, are plotted against the substrate ratios as in Figure 1,[11] their slopes are the relative reactivity of methylsilane and silane toward whatever intermediates X give rise to these "silylene products". The observed ratio 1.32 ± 0.04 is in good agreement with the ratios $k_1$:$k_2$ measured by Paquin and Ring at high temperatures (Scheme II) but is too large to be reconciled with their differential activation parameters.[10]

**Scheme II**

$$SiH_3SiMe_3 \xrightarrow{\Delta} SiH_2 + SiHMe_3$$

$$SiH_2 + SiH_3Me \xrightarrow{k_1} SiH_3SiH_2Me$$

$$SiH_2 + SiH_4 \xrightarrow{k_2} SiH_3SiH_3$$

The reactivity ratios $k_1$:$k_2$ found by Paquin and Ring to vary from 1.30 at 287 °C to 0.967 ± 0.05 at 246 °C could be extrapolated to 0.044 at 25 °C.

We have varied the recoil reaction parameters, and the resulting data have led to several conclusions: (1) From 27 to 202 °C the reactivity ratio is constant within experimental error. (2) The presence of a 7-fold excess of argon or a $12^1/_2$-fold excess of ethane, both inert moderators, also leaves the reactivity ratio unchanged. Hence intermediate X carries little, if any, excess kinetic or vibrational energy.[12] (3) Xenon, an inert "spin

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[†] This paper is dedicated to Professor William von Eggers Doering whose inspiration fuels so much of chemistry.

(1) Gaspar, P. P.; Pate, B. D.; Eckelman, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 3878.

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(3) Gaspar, P. P.; Markusch, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1331.

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(5) Gennaro, G. P.; Su, Y.-Y.; Zeck, O. F.; Daniel, S. H.; Tang, Y.-N. *J. Chem. Soc., Chem. Commun.* **1973**, 637.

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(7) Zeck, O. F.; Su, Y.-Y.; Gennaro, G. P.; Tang, Y.-N. *J. Am. Chem. Soc.* **1974**, *96*, 5967.

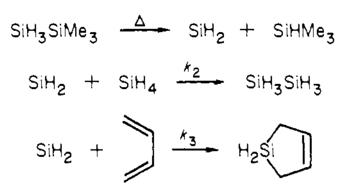
(8) Phosphine is the precursor of the recoiling silicon atoms, the phosphorus atom undergoing the $^{31}P(n,p)^{31}Si$ nuclear transformation with sufficient recoil energy to liberate the newly born silicon atom. For details of the recoil chemistry see ref 2, 4, and 9.

(9) Hwang, R.-J.; Gaspar, P. P. *J. Am. Chem. Soc.* **1978**, *100*, 6626.

(10) Paquin, D. P.; Ring, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 1793.

(11) The combined absolute yields of $^{31}SiH_3SiH_2Me$ and $^{31}SiH_3SiH_3$ totaled 40–50% at room temperature in mixtures containing 500 torr $PH_3$ and 500 torr $SiH_3Me$ + $SiH_4$.

Scheme III



converter", does not significantly affect the reactivity ratio when present at mole fractions of 0.93 and 0.96. Nitric oxide, an efficient free radical scavenger, also has little effect, either in the presence or absence of argon moderator. Hence it is unlikely that intermediate X is reacting in an excited electronic state or in any triplet state. (4) The reactivity ratio also remains unaltered in the presence of trimethylamine, whose ionization potential is lower than that of atomic silicon.[13] Therefore X is probably not cationic.

That X of Scheme I is indeed $^{31}SiH_2$ has been established beyond doubt by reinvestigating the competition for thermally generated silylene. When the static pyrolysis carried out by Paquin and Ring (Scheme II)[10] was instead carried out in a single-pass flow system over a 75-deg temperature range from 385 to 460 °C, no variation in the ratio, $k_1{:}k_2$ was found, and the values observed,[14] 1.38 ± 0.05, 1.35 ± 0.05, and 1.40 ± 0.05, agreed well with the reactivity ratio 1.32 ± 0.04 found in the recoil experiments. Thus the product-forming intermediates in the recoil reactions display the same temperature-independent relative reactivity toward silane–methylsilane mixtures as thermally generated singlet $SiH_2$.[15]

Evidence has also been found indicating that nucleogenic $SiH_2$ is relaxed to the ambient temperature. In a second series of flow pyrolysis experiments silane and butadiene were allowed to compete for thermally generated $SiH_2$.[16]

A small but systematic and reproducible variation in the reactivity ratio $k_2{:}k_3$ from 1.37 ± 0.05 to 1.05 ± 0.05 over the temperature range 377–470 °C was observed.[17,18] An Arrhenius plot (Figure 2) is reasonably linear, with correlation coefficient 0.984, $E_a{}^2 - E_a{}^3 = -2.6 \pm 0.3$ kcal/mol[19] and $A_1/A_2 = 0.18 \pm 0.03$, and leads to an extrapolated value at room temperature of $k_2{:}k_3 = 13 \pm 4$, which is similar to the reactivity ratio 9 ± 1 obtained in a recoil experiment.[9]

Thus at long last quantitative agreement has been found between the relative reactivity of an important product-forming intermediate formed from high-energy silicon atoms in mixtures containing labile hydrogen and ground-state singlet silylene. On the basis of this agreement the one can be identified with the other.

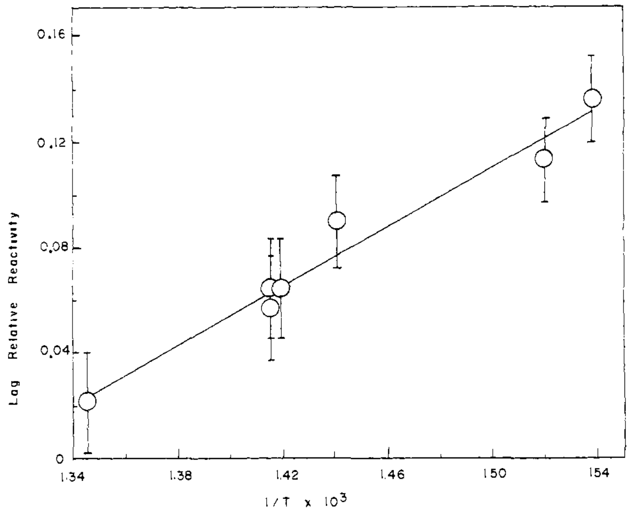


**Figure 2.** Temperature dependence of the relative reactivity of silane and butadiene toward thermally generated $SiH_2$, $k_2{:}k_3$, for the formation of $SiH_3SiH_3$ and 1-silacyclopent-3-ene in copyrolysis of mixtures of $SiH_3SiMe_3$, $SiH_4$, and butadiene.

It has furthermore been possible to measure, for the first time, the temperature of a polyatomic intermediate in a recoil reaction, and it was found that nucleogenic silylene reacts at its ambient temperature. Finally one must reject an earlier suggestion, based on a reduction of product yields in the presence of free radical scavenger, that nucleogenic silylene reacts principally in a triplet electronic state.[7] In the present experiments the *relative* reactivity is unaltered as product yields are decreased, and thus the effect of scavengers is on a species that appears earlier in the reaction sequence initiated by silicon atoms than the ultimate silylene intermediates.

**Acknowledgment.** This work received financial support from the United States Department of Energy. This is Technical Report COO-1713-111.

**Registry No.** $^{31}Si$, 14276-49-4; $^{31}SiH_2$, 53971-28-1; $SiH_4$, 7803-62-5; $SiH_3Me$, 992-94-9; butadiene, 106-99-0.

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(12) The absolute yields of disilane and methyldisilane are reduced by 40–50% in these moderator experiments.

(13) Ionization potentials: Si, 8.151 eV, (Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions" *NSRDS-NBS* **1969**, *26*, 162); $Me_3N$, 7.95 ± 0.10 eV (Rosenstock, H. M.; Sims, D.; Schroyer, S. S.; Webb, W. J. "Ion Energetics Measurements" *NSRDS-NBS* **1980**, *66* (Part I), 86).

(14) The flow pyrolyses were carried out at pressures of 15–25 torr and contact times of ca. 0.1 s. Reaction mixtures contained 0.65 mmol of $SiH_3SiMe_3$ and 23.5 mmol of $SiH_4 + SiH_3Me$, varying in ratio from 4:5 to 5:4, with 26–58% decomposition of $SiH_3SiMe_3$.

(15) There was already an indication in the photochemical experiments of Davidson that the selectivity of dimethylsilylene ($:SiMe_2$) toward Si–H insertion does not vary with temperature: Davidson, I. M. T.; Lawrence, F. T.; Ostah, N A. *J. Chem. Soc., Chem. Commun.* **1980**, 859.

(16) The reaction conditions were the same as those of ref 14, with reaction mixtures containing 0.65 mmol of $SiH_3SiMe_3$ and 26 mmol of $SiH_4 + C_4H_6$ in ratios from 3:5 to 3:2, with conversion of $SiH_3SiMe_3$ from 14% to 80%.

(17) It should be noted that this directly determined relative reactivity of silane and butadiene is in excellent agreement with a previous estimate based on an indirect comparison, footnote 42, ref 9.

(18) From results of shock tube experiments, a relative reactivity for butadiene and trimethylsilane of *1.0 ± 0.3* at *930 K* has been estimated: Dzarnoski, J.; Rickborn, S. F.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1982**, *1*, 1217.

(19) The higher activation energy for silacyclopentene formation is likely to be due to the rearrangement of an initial adduct, a vinylsilacyclopropane: Hwang, R.-J.; Conlin, R. T.; Gaspar, P. P. *J. Organomet. Chem.* **1975**, *94*, C38. The present results with $SiH_3Me$–$SiH_4$ mixtures suggest that the energy barrier for $SiH_2$ insertion into an Si–H bond is small; this has already been suggested for $SiMe_2$.[15]

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## Nickel-Promoted Thermal Dimerization of 1-Phenyl-3,4-dimethylphosphole: The First Synthesis of a Diphospholene

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*Received September 23, 1983*

Pursuing our interest[1-3] in the novel reactions of phospholes, we have investigated the thermolysis of 1-phenyl-3,4-dimethylphosphole in the presence of nickel(II) chloride. We have previously shown[3] that 1-phenylphospholes rearrange at high tem-

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(2) Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1982**, *104*, 2077.

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