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THE UNIVERSITY OF ALBERTA

THE PHOTOCHEMISTRY OF SILICON HYDRIDES

BY

THOMAS LONG POLLOCK

A THESIS

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FACULTY OF GRADUATE STUDIES

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ABSTRACT

The gas phase $Hg(6^3P_1)$ sensitization and direct photolysis of disilane and the $Hg(6^3P_1)$ sensitization of phenylsilane molecules have been investigated in detail. The primary processes and ensuing secondary reactions of the various silicon radicals have been elucidated.

The initial step in the mercury sensitization of Si_2H_6 and Si_2D_6 was found to involve only Si-H bond cleavage. The hydrogen atoms undergo a novel displacement reaction with disilane as well as the more common abstraction reactions. Scavenging studies with ethylene and nitric oxide coupled with isotopic substitution have shown that disilanyl radicals either combine in the presence of a third body or disproportionate to disilane and a diradical species. Monosilyl radicals only disproportionate to silane and silylene at pressures below one atmosphere.

The mercury photosensitized decomposition occurs with unit efficiency at room temperature and a temperature study indicated that the monoradicals were stable with respect to homogeneous decomposition up to 220°C. The monosilyl radicals abstract from the disilane substrate and the disilanyl radicals displace a silyl radical from disilane at elevated temperatures.

The mercury photosensitization of phenylsilane resulted in near unit decomposition at room temperature and above. The major step was found to be Si-H bond cleavage. Two other processes, C-Si scission and elimination of SiH_2 contributed about 20% between them. Isotopic substitution studies showed that monosilane was formed by the abstraction of hydrogen atoms from the silyl side chain by SiH_3 at 105°C.

The mechanism of the near ultraviolet photolysis of disilane was deduced from the effect of exposure time, pressure and radical scavengers on the product yields. Molecular elimination processes predominated over single bond homolyses in this system. Both SiH_4 and H_2 were primary products. Molecular hydrogen was formed from both 1,1 and 1,2 elimination. The silylenes SiH_2 and SiH_3SiH inserted into substrate to give trisilane and tetrasilane while SiH_2SiH_2 was the polymer precursor. The contribution to the overall decomposition of Si-H and Si-Si scissions was less than ten per cent.

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CHAPTER I

INTRODUCTION

I. SOME ASPECTS OF SILICON CHEMISTRY

The chemistry of silicon is a dynamic, rapidly expanding field. In 1964 one hundred and eighty references were considered sufficient to give a review of the work being done in organosilicon chemistry. By 1967 more than four times as many references, eight hundred and sixty-five, were required for a similar review in the fledgling series Organometallic Chemistry Reviews. Admittedly most of the work is of a preparative nature but the scattered references to mechanistic and kinetic studies are becoming more frequent, and tend to emphasize the differences between carbon and silicon chemistry. What is the physical basis for these differences?

Carbon and silicon atoms both have ^3P ground states which, in simple valence-bond theory, may be represented as (ns^2np^2) where n = 2 for carbon and 3 for silicon. Silicon has vacant 3d orbitals which lie 130 kcal/mole above the highest occupied orbitals whereas the 3d orbitals in carbon are 220 kcal/mole above the 2p orbitals (1). The five-fold degenerate d-orbitals of silicon are available for bonding then since energetically it is more favourable to promote a 3p electron to a 3d

orbital than to promote one of the paired 3s electrons to a 3p orbital, 130 kcal/mole vs 139 kcal/mole. Rather drastic conditions are necessary for silicon to expand its valency to six; strongly electron-withdrawing ligands such as fluorine are able to contract the diffuse d orbitals sufficiently to permit the existence of the compound K_2SiF_6.

Another role of the d-orbitals in silicon is in internal (p_π - d_π) bonding. While the existence of this type of bonding is generally agreed upon, its strength is still under debate (2). To list only a few of the phenomena which could be attributed to (p_π - d_π) bonding one can mention the following:

The electron density withdrawal from the aromatic ring in silylsubstituted benzenes (3).

The interaction between the silicon atom and the half filled p-orbital in the $(CH_3)_3Si\text{-}\dot{C}H_2$ radicals (4).

The various peculiarities in the near u.v. spectra of extended chain and cyclic silanes (5,6).

The vacant 3d orbitals of silicon then may be utilized for external bonding as in the hexavalent silicon salts, internal (p_π - d_π) bonding in either the ground or excited electronic state, or as a low-lying multi-directional path for both heterolytic and homolytic attack on silicon atoms (7). Thus these orbitals serve to modify slightly the chemistry of the normal sp^3

hybridization common to both carbon and silicon.

Though sp^3 hybridization is common to both families, stable examples of sp^2 and sp hybridization in silicon chemistry are unknown. This is also seen in the physical properties of the free radicals derived from silicon. The unpaired electron on monosilyl radicals, trapped at 4°K, retains 21% of its s character and the radical retains its pyramidal configuration in contrast to the methyl radical in which the electron is in a p-orbital and the radical is planar (8-12). The ground state of $:SiH_2$ has recently been found to be a bent singlet (13,14), again in contrast to the linear triplet ground state of $:CH_2$ which can be said to represent sp hybridization of the carbon electrons. It is concluded then that silicon is either sp^3 hybridized or else not hybridized at all, i.e. divalent.

Divalent silicon species have been predicted to possess some degree of stability (15,16). Difluorosilylene has a half-life of approximately 150 seconds at ambient temperatures and 0.1 torr (17). As a consequence of this stability silicon compounds have the avenue of molecular elimination open to them in their decomposition reactions

$$R_4Si \longrightarrow R - R + :SiR_2 \qquad [1]$$

and indeed the high temperature decomposition of silicon

halides has proven to be one useful source of halo-silylenes (18).

Silicon is less electronegative than most of the atoms with which it commonly combines (19). As a consequence, the hydrogen of the silicon-hydrogen bond is hydridic and carbon carries the partial negative charge in the charge separation of the silicon-carbon bond. Heterolytic cleavage of the bonds to silicon therefore proceeds more readily than in carbon chemistry. Trends in homolytic cleavage of these same bonds are rather more difficult to predict.

Some bond enthalpies are listed in Table I where it can be seen that silicon-silicon and silicon-hydrogen bonds are weaker than the corresponding carbon linkages but the bond enthalpies for silicon and Group V, VI and VII atoms are greater than those for carbon and these atoms. Individual bond dissociation energies and best estimates for the heats of formation of some silyl compounds of interest are given in Table II.

II. SILYL RADICALS

In view of the foregoing discussion and the increasing stability of divalent species as one descends the Group IV atoms from C to Pb reaction path [2]

$$MR_4 \longrightarrow :MR_2 + R_2 \qquad [2]$$

TABLE I - I

Some Bond Enthalpies (kcal/mole) for MX

X	C	Si
H	99.2[a]	77.4 (SiH_4)[b]
C	82.6[a]	73.2 (Me_3SiCl)[c]
N	72.8[a]	76.4 [$(Me_3Si)_2NH$][c]
O	85.5[a]	106.3 [$(Me_3Si)_2O$][c]
F	116 (CF_4)[a]	142 (SiF_4)[d]
Cl	81 (CCl_4)[a]	97.2 ($SiCl_4$)[d]
Br	68 (CBr_4)[a]	75.6 ($SiBr_4$)[d]
I	51 (CI_4)[a]	56 (SiI_4)[d]
Si	73.2[b]	64 (Si_2H_6)[b]

a) T. L. Cottrell, "Strengths of Chemical Bonds", Butterworth, London, 2nd ed., 1958.

b) Based on ΔH_f^o (gas)[e] of SiH_4 = 7.3; Si_2H_6 = 17.1; Si = 108.9; H = 52.1 (kcal/mole).

c) A. E. Beezer and C. T. Mortimer, J. Chem. Soc. (A), 514 (1966).

d) A. E. Beezer and C. T. Mortimer, J. Chem. Soc., 2727 (1964).

e) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards Technical Note 270-3, U.S. Government Printing Office, Washington D.C., 1968.

TABLE I - II

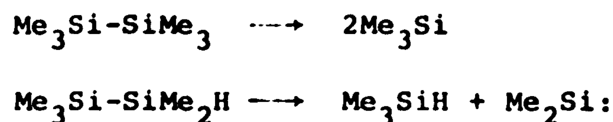
Some Bond Energies and $\Delta H^{\circ}_{f(g)}$ for R-X (kcal/mole)

R-X	ΔH°_{f} (R)	Ref.	D(Bond)	Ref.
H_3Si-H	50	(20)	94	(21)
H_2Si-H	-			
$HSi-H$	87	(22)		
$Si-H$	109		74	(22)
$H_3Si-SiH_3$	50	(20)	81	(21)
H_5Si_2-H	-		90	(23)
$(Me)_3Si-H$	-26	(24)	81	(24)
$(Me)_3Si-H$	9	(25)	70	(25)
$(Me)_3Si-Cl$	-26	(24)	88	(24)
	9	(25)	123	(25)
$(Me)_3Si-Br$	-26	(24)	79	(24)
$(Me)_3Si-I$	-26	(24)	69	(24)
$(Me)_3Si-Me$	-26	(24)	75	(24)
	9	(25)	75	(25)
$(Me)_3Si-Si(Me)_3$	-26	(24)	67	(24)
	9	(25)	67	(25)

may be expected to successfully compete with single bond homolysis

$$MR_4 \rightarrow \cdot MR_3 + R \qquad [3]$$

in the pyrolysis of silanes. This competition is demonstrated in the thermolyses of hexamethydisilane and pentamethyldisilane (26-33) where the primary steps are



$$Me_3Si\text{-}SiMe_3 \rightarrow 2Me_3Si$$

$$Me_3Si\text{-}SiMe_2H \rightarrow Me_3SiH + Me_2Si:$$

and emphasizes the care with which potential silyl radical sources must be chosen.

A. Production of free radicals

(i) Pyrolysis

(a) Monosilane and its derivatives:

The thermal homolytic cleavage of covalent hydrogen bonds to silicon has been used as a source of silyl radicals. There exists some controversy as to whether the primary step in the pyrolysis of monosilane is analogous to [2] or [3] (34-37). Purnell and Walsh (36) favour the split into molecular hydrogen plus silylene. Ring et al. (37) favour the initial cleavage of a single Si-H bond. They cite the formation of HD in an SiH_4 - SiD_4 mixture as being evidence for this mode of decomposition but fail to report their yield of hydrogen. It has also been observed that a mixture of GeH_4 and GeD_4

produces HD on pyrolysis but this reaction was complicated by surface effects and it was concluded that germane decomposed via pathway [2] (38,39).

In support of reaction pathway [3] White and Rochow (40) found ethylsilane and vinylsilane respectively when silane was pyrolysed in the presence of ethylene and acetylene. This however, probably indicates no more than the presence of free radicals in the system since they observed extensive polymerization on the walls of the reaction vessel.

These conflicting opinions on the nature of the initial step have given rise to two theoretical interpretations based on the stability of silylenes or a modification of the reaction path by d-orbitals. The proponents of primary step [2] consider disilane as being formed by insertion of the initially formed ground-state singlet silylene into a silicon-hydrogen bond of silane. In the second case the monosilyl radical from the initial step approaches a substrate molecule on a potential surface modified such that it loses one of its hydrogen atoms and then forms disilane.

A greater number of studies have been done on the pyrolysis of alkyl silanes but most of them have been of an exploratory nature. Tetramethyl silane decomposes at an appreciable rate only above 650°C (41). The

activation energy was measured at 79 kcal/mole but the products are not simple so it is not possible to equate this value with the carbon silicon bond in $(CH_3)_4Si$ (42). Trialkyl silanes have been reported to decompose more rapidly than the tetraalkyls at the same temperature (43, 44). The fact that these pyrolyses are indubitably chain reactions only reflects the presence of a Si-H bond which is more easily abstracted than a C-H bond and does not necessarily mean that D(≡Si-H) is less than D(≡Si-C).

(b) Compounds containing Si-Si bonds:

Disilane and hexamethyldisilane have been the subject of numerous investigations. Early studies on disilane established that the decomposition obeyed first-order kinetics with an activation energy of 49-51 kcal/mole (45,46). A free radical mechanism has been postulated. More recent investigations of the pyrolysis of disilane however indicate that the primary step is decomposition to form a silane molecule plus silylene. The silylene then inserts into the silicon hydrogen bond to give the product trisilane which is equal to the monosilane when decomposition is restricted to less than one _per cent_ (47-49).

Substituted disilanes may also decompose by path [2]. Pentamethyldisilane yields trimethylsilane and dimethylsilane (33). This same type of reaction is

well characterized for methoxy substituted disilanes and has been observed for $Me_3SiSiMe_2X$ where X = Cl,OPh,Ph (18).

In contrast, hexamethyldisilane has been found to undergo homolysis of the silicon-silicon bond (26-32).

Well-known sources of carbon radicals such as azocompounds, metal alkyls and peroxides have not proved to be useful sources of silyl radicals. Substituted silyls of the type $R_3Si-N=N-SiR_3$ have been prepared but decompose to give $(R_3Si)_2N-N(SiR_3)_2 + N_2$ rather than $(R_3Si)_2 + N_2$ (50). Similarly substituted silyl mercurials have been prepared but their thermal decomposition in solution to give silyl radicals has been questioned. It appears that the mercurials undergo a molecular reaction (51-54).

(ii) <u>Photolysis</u>

The simple hydrides and organic derivatives of silicon do not absorb in the near ultraviolet. Mercury photosensitization provides a means of achieving reaction and has been reported for silane (55,56), the methylsilanes (56) and the chlorosilanes (57,58).

In all cases silicon-hydrogen bond cleavage occurred if one was present. In tetramethylsilane carbon-hydrogen bond cleavage took place instead. No reaction occurred with tetrachlorosilane. Monosilane

sensitization must include additional steps since in a fresh reaction vessel hydrogen is produced with a quantum yield of ten but decreases to three in a used cell. Reedy (58) also employed various organic sensitizers and found no reaction when trimethylsilane was photosensitized with benzene. This indicates that $D(Me_3Si-H) \geq 83$ kcal/mole.

Linear (5) and cyclic (6) polysilanes absorb in the near ultraviolet. Dodecamethylcyclohexasilane is reported to undergo ring contraction on photolysis to give permethylcyclopentasilane plus dimethylsilylene (6).

The onset of absorption of silane and the methyl silanes in the vacuum-ultraviolet is red-shifted from the simple alkanes (59). The importance of initial decomposition to silylene or a methyl-substituted silylene has been unequivocally demonstrated through the use of nitric oxide scavenging and isotopic labelling studies in the 123.6 nm and 147 nm photolysis of methylsilane (60,61). Subsequent work on the vacuum ultra-violet photolysis of dimethylsilane and disilane (62) as well as monosilane (63) has provided further examples of the universal nature of this process. The silylenes insert into a silicon-hydrogen bond of the substrate to give vibrationally excited disilanes which can be pressure stabilized.

Other examples of direct photolysis include the flash photolysis of chloro- and bromosilane to give molecular hydrogen plus the monohalosilylene (64) and the vacuum ultraviolet photolysis of silane and its halogen derivatives using a hydrogen discharge (65-68). Aromatic substitution on the silicon atom makes it amenable to absorption in the near ultraviolet. While it was possible to observe a weak spectrum of SiH_2 from the flash photolysis of phenylsilane (69) less drastic conditions with diphenylsilane produced a redistribution of the phenyl groups via participation of silyl radicals (70).

$$4\phi_2SiH_2 \xrightarrow{h\nu} \phi_4Si + \phi_3SiH + \phi\text{-}SiH_3 + SiH_4$$

The most convenient photolytic source of silyl radicals in solution to date has been the photolysis of the bis(trialkylsilyl) mercury compounds (53,71,72).

(iii) Metathesis

A technique used extensively in preparative work is the free radical initiated chain addition of silyl radicals to unsaturated compounds. The most common initiators are t-butyl peroxide and azoisobutyronitrile.

$$R_3SiH + R' \longrightarrow R'H + R_3Si$$

Only catalytic amounts of initiator are required and

side reactions between the initiator and the silyl radicals are thus minimized.

Recently several kinetic studies on the alkyl free radical metathetical reactions with silanes and substituted silanes have been reported (23,73-86). In all cases the rate of abstraction was greater for the silane than for the corresponding carbon compound. It has now been established (23,73-75,77,78) that the increase in reactivity is due to the lower activation energy for the abstraction reaction, the A-factors being similar for both carbon and silicon compounds.

The thermal reaction between hexamethyldisilane and iodine proceeds by a S_H2 mechanism rather than by abstraction of a hydrogen atom as is the case for alkanes (87).

$$I + Me_3Si\text{-}SiMe_3 \longrightarrow Me_3SiI + Me_3Si$$

This type of reaction is common for elements possessing vacant d-orbitals (88).

(iv) Other Methods

Radiolysis and electric discharges have also been employed to produce silyl radicals (63,89,90). Because of the high energy of the radiation, indiscriminate breaking of the various bonds usually occurs, giving rise to a wide variety of products.

B. Removal of free radicals

Organic free radicals undergo three broad classification of reactions:

(i) Unimolecular reactions
   a) isomerization
   b) decomposition

(ii) Radical-Molecule reactions
   a) addition to unsaturated molecules
   b) abstraction or radical transfer

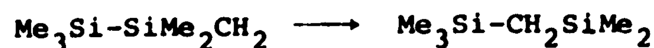
(iii) Radical-Radical reactions
   a) combination
   b) disproportionation

These reactions have been the topic of several review articles (91). Silyl radicals will be considered under the same classifications.

(i) Unimolecular Reactions

Kinetic studies on the isomerization and decomposition of silyl radicals are non-existent. There are some qualitative observations which indicate that the permethylsubstituted radicals are more stable toward unimolecular decomposition or isomerization than the corresponding alkyl radicals. Trimethylsilyl radicals are stable up to 400°C (56). These radicals are produced in the homolysis of hexamethyldisilane and are postulated to undergo only combination or abstraction

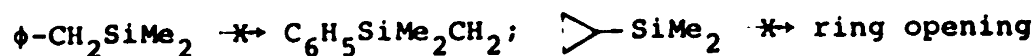
reactions at low pressures and 550°C (30). At pressures higher than 1 torr and temperatures 400-600°C the decomposition of hexamethyldisilane is complicated by chain reactions and the various steps are uncertain (26-32). The radical produced when trimethylsilyl abstracts from hexamethyldisilane, while not a silyl-radical itself, does rearrange to a silyl radical at pyrolysis temperatures (92).



$$Me_3Si\text{-}SiMe_2CH_2 \longrightarrow Me_3Si\text{-}CH_2SiMe_2$$

No isomerization took place at 80°C.

Two other examples of the stability of silyl radicals under conditions where carbon radicals are known to isomerize are the benzyldimethylsilyl (70) and cyclopropyldimethylsilyl (93) radicals at 140°C.

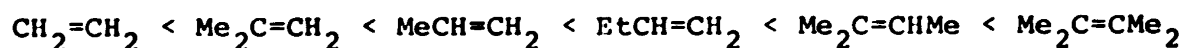


$$\phi\text{-}CH_2SiMe_2 \not\rightarrow C_6H_5SiMe_2CH_2; \quad \triangleright\text{-}SiMe_2 \not\rightarrow \text{ring opening}$$

(ii) Radical-Molecule Reactions

The addition of silyl radicals to double bonds is one of the major laboratory sources of organosilicon compounds (94). Addition to terminal alkenes is anti-Markovnikov. The silicon hydride is such an efficient chain transfer reagent that the monomer can be used to characterize the free radical in the system (40,89). In spite of, or because of, the extensive use of this reaction

for synthesis almost no kinetic studies have been done. The relative rates of the thermal addition of trichlorosilane to ethylene and methyl-substituted ethylenes suggest that the trichlorosilyl radical is electrophilic (95):



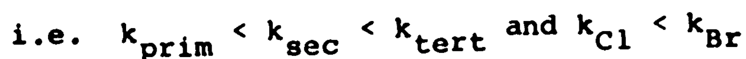
$$CH_2{=}CH_2 < Me_2C{=}CH_2 < MeCH{=}CH_2 < EtCH{=}CH_2 < Me_2C{=}CHMe < Me_2C{=}CMe_2$$

Silyl radicals may abstract from saturated compounds. There exists an empirical relation, after Polanyi, between the enthalpy change for an abstraction reaction and the activation energy of the same (96). Hydrogen abstraction by silyl radicals is expected to be slower than for the corresponding alkyl radicals because of the lower Si-H bond energy. Trimethylsilyl radicals produced by the photolysis of bis(trimethylsilyl)mercury in anisole, xylene and toluene produced only small amounts of trimethylsilane - less than 1% of the mercurial which had decomposed (97). Pentamethyldisilyl reacted with toluene at 135°C to give addition and recombination products. Bibenzyl accounted for about 8% of the toluene which had reacted (98). A material balance in the published data suggests that the benzyl radicals were largely produced by abstraction by the initiator.

At the temperature used for the pyrolysis of hexamethyldisilane, however, abstraction of hydrogen

from the substrate can compete effectively with combination of the free radicals in the system (32).

Abstraction of halogen atoms from halo-carbons by silyl radicals is exothermic and has been reported by several workers (99-113). The abstraction from alkylchlorides and bromides by $SiCl_3$ has been shown to be a straightforward chain reaction in which the relative rates for a series of normal and branched alkyls accurately reflect the energy of the bond being broken (112,98).



i.e. $k_{prim} < k_{sec} < k_{tert}$ and $k_{Cl} < k_{Br}$

The same reactivity was found for triethyl and diphenylmethylsilyl radicals reacting with a series of halogen-substituted hydrocarbons (103-105). Carbon tetrachloride was found to be the most reactive among the chlorinated hydrocarbons and it has been used to demonstrate that a silyl radical derived from an optically active silane retains its optical activity (106). Carbon tetrachloride also competes effectively with phenyl-substituted silanes for silyl radicals (101,105), which in the absence of CCl_4 undergo redistribution (70).

The reactivity of Me_nSiCl_{3-n} when n = 0-3 toward primary and secondary C-Cl bonds has been established as $Me_3Si > Me_2SiCl > MeSiCl_2 > SiCl_3$ (107,108). Bearing in mind that the free electron in $\cdot SiH_3$ retains

21 per cent s character and that there is evidence that this decreases with methyl substitution (8-12) it would seem that a correlation exists between the degree of s character of the unpaired electron and the selectivity of the radical.

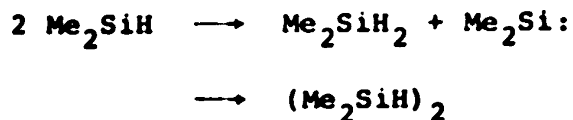
Aryl halides are subject to abstraction reactions (109-113) as well as the more familiar substitution reactions. Curtice et al. (109) found no evidence for a chain reaction when triphenylsilyl radicals, formed by a peroxide initiator, abstracted chlorine from chlorobenzene. The resultant phenyl radicals appeared as chlorobiphenyls in the products along with the triphenylchlorosilane. Sakurai et al. (111), however, favour the homolytic substitution mechanism for the peroxide initiated reaction between triethylsilane and chlorobenzene since they found no chlorobiphenyls among the products, only hexaethyldisiloxane, benzene and phenyltriethylsilanes. Davidson et al. (110) have shown that the thermal gas-phase reaction between trichlorosilane and chlorobenzene proceeds via two distinct chain mechanisms. The one leads to the condensation product phenyltrichlorosilane plus hydrogen chloride and the other, the abstraction reaction, to trichlorosilane and benzene. A preliminary investigation by the same authors of the trimethylsilane plus chlorobenzene reaction was complicated by secondary processes, such as the cleavage of

trimethylphenylsilane by hydrogen chloride to give benzene and chlorotrimethylsilane. The same parallel processes are probably occurring in the peroxide initiated reactions and would explain the differing results of the two groups in the liquid phase.

(iii) Radical-Radical Reactions

Free radicals usually disappear from a system by either combination or disproportionation. Silyl radicals, because they don't form stable $p_{\pi} - p_{\pi}$ bonds, would not be expected to form the analogous disproportionation products of alkyl radicals, i.e. silane and nonexistent silene. On the other hand it might be possible for them to follow another disproportionation path to yield a saturated molecule and a diradical intermediate.

Trisubstituted silyl radicals have been found to give only recombination products when they are the only radicals in the system (56-58). Disproportionation of the trimethylsilyl radicals to tetramethylsilane and dimethylsilylene is apparently unfavourable. Such is not the case for mono- and dimethylsilyl radicals. Some processes other than dimerization must be occurring and disproportionation is a plausible alternative (56,114).



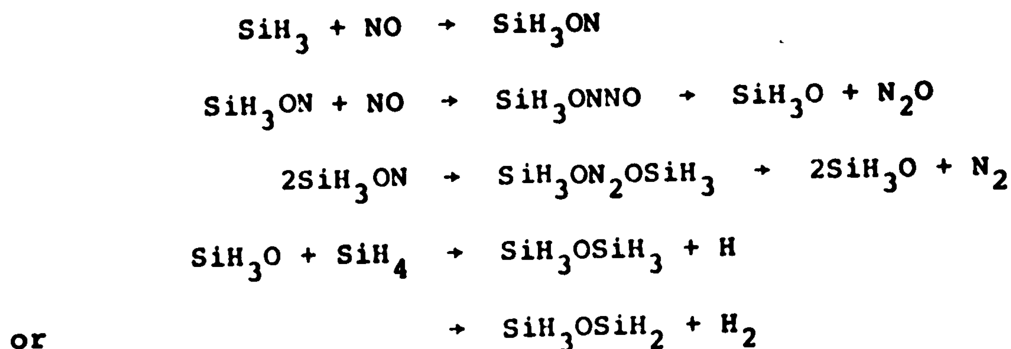
$$2\ Me_2SiH \longrightarrow Me_2SiH_2 + Me_2Si:$$

$$\longrightarrow (Me_2SiH)_2$$

This alternative reaction is more important for monomethylsilyl radicals than for dimethylsilyl radicals. A logical extension of this trend is that combination of unsubstituted monosilyl radicals may be less favourable than disproportionation to give silane and silylene. In fact when silyl radicals were formed in the presence of excess methyl radicals the products could be rationalized only if the predominant reaction between methyl and silyl afforded methane plus silylene (115). The silylene could then combine or disproportionate further when the methyl radicals to give di- and trimethylsilane.

Hydrogen atoms were reacted with a mixture of SiH_4 and SiD_4 to give monosilyl and monosilyl-d_3 radicals (62). Mixed disilanes were formed in which the major components were d_o, d_2, d_4, d_6 in support of disproportionation, followed by insertion of the silylene into the Si-H bonds to give the observed disilanes.

Substituted and unsubstituted silyl radicals react efficiently with the stable free radical nitric oxide (56,116,117) to produce siloxanes and nitrous oxide as the principal products. At room temperature the reaction is a chain reaction and produces nitrogen and hydrogen as well. The mechanism has not been elucidated but the best available data indicate that the silyl radical reacts with the oxygen end of NO (56,117):



$$SiH_3 + NO \rightarrow SiH_3ON$$

$$SiH_3ON + NO \rightarrow SiH_3ONNO \rightarrow SiH_3O + N_2O$$

$$2SiH_3ON \rightarrow SiH_3ON_2OSiH_3 \rightarrow 2SiH_3O + N_2$$

$$SiH_3O + SiH_4 \rightarrow SiH_3OSiH_3 + H$$

or

$$\rightarrow SiH_3OSiH_2 + H_2$$

III. SILYLENES

In that body of literature concerned with the kinetic and mechanistic aspects of free radicals derived from silicon there is an increasing awareness of the importance of divalent silicon intermediates. Many of the methods utilized for production of monoradicals may also give the diradical, silylene. Why, then, were the silylene intermediates not characterized sooner? The answer lies in their chemistry. This has recently been reviewed by Atwell and Weyenberg (18) so that this discussion will be confined to the gas phase work.

Silylenes generated in the absence of other reagents polymerize. Difluorosilylene has been extensively studied by Margrave and co-workers (118). This polymerization is not confined to the halosilenes however; polymers variously described as "non-volatile viscous liquids" or "white polymeric films", depending

on the substituents, are products of the reaction of all free radicals.

Skell and Goldstein (16) postulated that dimethyl silylene inserts into the silicon-hydrogen bond of trimethylsilane. This is a characteristic reaction of silyl silylenes and alkylsubstituted silylenes (60,61). A series of competitive reactions has been established that at the pyrolysis temperature of disilane, the rate of insertion of SiH_2 into Si-H bonds decreases in the order $Me_2SiH_2 > MeSiH_3 > Si_2H_6 > SiH_3Cl$ (49). In a parallel study Bowrey and Purnell (48) found that SiH_2 from the pyrolysis of Si_2H_6 inserted into the Si-H bond of mono-, di-, and trisilane. No reaction was found with either tetramethyl silane or the alkanes, ethane and propane. Thus we can say that silylene is an electrophilic reagent and that there exists an energy barrier for insertion into primary and secondary carbon-hydrogen bonds which is greater than that for insertion into Si-H bonds of disilane. In addition, there is no evidence for insertion at C-Si bonds or Si-Si bonds (16,47-49,60-62,119).

Silicon-hydrogen bonds are not the only ones reactive toward silylenes, as has been shown by condensed phase work. In this medium "the insertion of silylenes into a variety of MX bonds (where M represents boron, carbon or phosphorus and X represents halogen or alkyoxy) may be a rather general reaction" (18).

Diphenyl acetylene is an effective radical trap for silylenes formed in the condensed phase, where the initially formed silacyclopropene dimerizes to give a 1,4 silicon substituted cyclohexadiene. 1,3-Butadiene is just as effective as substituted acetylenes for trapping silylenes in solution and both of these linkages are more reactive toward silylenes than ethylene (18). No reactions between divalent silicon intermediates and acetylenes or 1,3 dienes have been reported in the gas phase. This can only be because no suitable system has been studied since dimethylsilylene reacts with ethylene go give vinyldimethylsilane (16). Contrast this with the vacuum ultraviolet photolysis of methylsilane where ethylene could not compete successfully with the substrate for the CH_3SiH and SiH_2 present in the system (60).

From the gas-phase work the order of reactivity of silylenes is

prim-CH and sec-CH $<$ C_2H_4 $<$ prim-SiH $<$ sec-SiH $<$ tert-SiH

and from condensed phase work we have

benzene $<$ ethylene $<$ dimethoxytetramethylsilane $<$ dienes and alkynes.

It should prove fruitful to add a diene or an alkyne to the disilane pyrolysis system.

Silylenes do not combine with the free radical nitric oxide. This proved to be useful in the elucidation

of the mechanism of the vacuum ultraviolet photolysis systems (60-62).

In conclusion silylenes insert into silicon-hydrogen bonds, add with facility to dienes and alkynes and are inert toward nitric oxide.

PRESENT INVESTIGATION

The complexity of the mercury-sensitization of monosilane as compared to the methyl-substituted silanes required that some other source of unsubstituted silyl radicals be found. Phenylsilane was a possible source. If, as was true for the alkylsilanes, only silicon-hydrogen bond fission took place the reactions of the aryl-substituted silyl radical could be compared to the alkyl-substituted radicals. It was also possible that silicon-carbon cleavage could occur. The extent of either of these processes would add to the understanding of energy transfer by excited mercury atoms.

Disilane has both Si-H and Si-Si bonds. Both of these bonds exhibit large quenching cross-sections in their collisions with excited mercury atoms (Table III). Elucidation of the reaction mechanism for the mercury sensitization of disilane, in addition to its intrinsic interest, should also provide information on the mode of transfer of energy from mercury to the polarizable bonds of silicon.

TABLE I - III

Quenching Cross Section Values of Silanes and Paraffins for Hg (6^3P_1) Atoms[a]

Silicon Compounds	σ_Q^2, A^2	Carbon Compounds	σ_Q^2, A^2
SiH_4	26	CH_4	0.06
$MeSiH_3$	32	C_2H_6	0.10
$(Me)_2SiH_2$	33	C_3H_8	1.5
$(Me)_3SiH$	30	$(Me)_3CH$	6.8
$(Me)_4Si$	5.0	$(Me)_4C$	1.4
$(Me)_3SiF$	1.0	C_6H_6[b]	39.4
$(Me)_2SiF_2$	0.19	C_6H_5Me[b]	59.1
$(Me)_6Si_2$	33		

(a) See reference (120).

(b) See reference (121).

In view of the facility of the metathesis between methyl radicals and the silanes it was felt that a study of the fate of the resultant silyl radicals would contribute to an understanding of their chemical reactions. It was postulated that since methyl radicals readily abstract from silanes, hydrogen atoms should also produce silyl radicals plus hydrogen molecules, and provide yet another source of silyl radicals.

The thermal stability of the silyl radicals was also studied.

The onset of absorption of disilane occurs at approximately 210 nm so it is possible to effect the direct photolysis using conventional photolysis techniques. The results of this study were contrasted with the mercury sensitization system.

CHAPTER II

EXPERIMENTAL

High Vacuum System

Pressures of 10^{-6} torr could be realized in a conventional high vacuum apparatus pumped by a three stage mercury diffusion pump backed by a Cenco Hyvac 7 oil pump. The apparatus was rendered grease free throughout by means of Delmar mercury float valves and Hoke metal diaphragm valves (numbers TY440, C413K and C415K). Absolute pressures were measured with a MacLeod gauge, a constant volume mercury manometer or an Octoil S (Consolidated Vacuum Corporation) manometer. Low temperature distillations and gas transfers were monitored on a Pirani Vacuum Gauge (Consolidated Vacuum Corporation, Type GP-140) utilizing Pirani gauge tubes (Consolidated Vacuum Corporation Cat. No. GP-001). Samples could be introduced into the attached inlet system of the gas chromatograph either through the Toepler pump - gas burette assembly or directly from the distillation train.

Photolytic Assembly

All experiments were carried out in a 60 x 50 mm cylindrical quartz cell equipped with a cold finger and attached to the vacuum system via a quartz to pyrex graded seal through a Hoke TY440 valve. For runs at

elevated temperatures the cell was surrounded by an insulated aluminum block furnace equipped with quartz end plates to minimize heat losses at the faces of the cell. Temperatures were determined with an iron-constantan thermocouple. Potentials were measured on a Leeds and Northrup potentiometer (Catalogue Number 8667).

The incident radiation was derived from two different sources, a low-pressure mercury resonance arc, Hanovia #687A45, and a medium pressure mercury arc, Hanovia Type 30620. For both sources provision was made for inclusion of appropriate wavelength and neutral density filters. The low-pressure arc had a Vycor envelope which effectively eliminated the 184.9 nm resonance line. This lamp was used as the source of the 253.7 nm mercury resonance line. The lines around 280, 265 and 195-205 nm in the medium pressure arc were utilized for various experiments.

Analytical System

Gas chromatography (g.c.) was the major analytical tool. It was used for identification, purification and separation of the reactants and products. Three different detection systems were used in the present study. The initial work was done with a Gow-Mac TR-II-B temperature regulated thermal conductivity cell maintained at 150°C and with a filament current of 250 mamp. The power supply

unit was a Gow-Mac 9999-C. This detector was subsequently replaced with a Gow-Mac Tr-III-A temperature regulated thermistor cell thermostated at 40°C. The power supply for this unit was a Gow-Mac 9999-D1 and was operated at 10 mamp. The chromatograms were displayed on a Sargent model RS recorder.

For these units the carrier gas was helium (single stream) which had passed through activated molecular sieve 13X in a spiral trap bathed in liquid nitrogen. The flow was regulated with an Edwards needle valve and was measured with a bubble flow meter. The 6 mm o.d. glass spiral columns packed with appropriate materials were maintained at the desired temperatures in an aluminum cylinder heated by suitably insulated resistance wire.

Typically, non-condensable gases were measured in the gas burette from where they could then be introduced directly into the evacuated sample loop of the g.c. or pass to a second Toepler pump equipped with a removable glass ampoule. The total amount of condensable product was measured in the gas burette then transferred to the g.c. sample loop. Separation was then achieved on a suitable column and the separated components could then be condensed from the detector outlet stream in the trapping train. From this trapping train the samples could be transferred directly to the high vacuum system

and containers suitable for mass spectral (m.s.), infra-red (i.r.) or nuclear magnetic resonance (n.m.r.) analysis.

The third detector used in this study was the hydrogen-flame ionization unit of a Hewlett-Packard 5750 Research Chromatograph. Sample introduction on this unit was somewhat different. Due to the inherent high sensitivity of this detector the entire reaction mixture, substrate plus product, was frozen into a pyrex ampoule equipped with a Burrell Silicone rubber seal. The pressure in the ampoule was raised to atmospheric with helium, added from a gas syringe, after which a suitable sample could be withdrawn in a syringe for injection onto the column of the gas chromatograph.

Unsubstituted silanes cause relatively rapid deterioration of the sensitivity of a hot wire detector. For this reason the total products were measured in the gas burette and the amount of each component was computed from the peak size and a relative response factor. This factor, determined from time to time remained constant at 1.23 per Si atom in the molecule.

Columns employed in this study are listed in Table IV.

Materials

The compounds used, their source, grade and purification are listed in Table V.

TABLE II - I

G.L.C. Retention Data and Operating Conditions

Column	Length feet	Temperature °C	Flow cc/min	Compounds Analyzed and Relative Retention Times		
Silicone Gum	20	130	40	benzene		0.35
Rubber SE-30 20% on				phenylsilane	10'08"	1.00
Diatoport-S 60/80 mesh				phenyldisilane		1.96
		74	50	monosilane		0.61
				disilane	3'41"	1.00
				trisilane		1.30
				tetrasilane		3.30
Silicone Oil DC710	20	85	60	monosilane		0.83
on Chromosorb W				disilane	3'13"	1.00
68/80 mesh				trisilane		1.66
				tetrasilane		4.14
				dimethyl mercury		8.28

TABLE II - I (cont'd)

Medium Activity Silica Gel	10	26	67	monosilane	2'23"	1.00
				ethane		1.23
				ethylene		1.86
				disilane		4.84
				n-butane		8.10
			60	nitric oxide		0.66
				monosilane	2'38"	1.00
				nitrous oxide		1.89
			50	methane		0.73
				monosilane	2'46"	1.00
				ethane		1.24
				methylsilane		2.70
Silicone Gum Rubber SE-30 20%	15	65-200 10°C/min	50	benzene		0.51
				phenylsilane	6'05"	1.00
				phenyldisilane		1.60
				diphenylsilane		3.12

TABLE II - I (cont'd)

Silicone Oil DC200 on Chromosorb W 60/80 mesh	10	49	60	monosilane		0.74
				disilane	2'15"	1.00
				$SiH_3OSi_2H_5$		2.02
				trisilane		2.23
				ethyldisilane		2.85
				C_4SiH_{12}		3.23
				$Si_3H_8O_3$		3.48
				$Si_4H_{10}O_4$		4.54
				$(Si_2H_5)_2O$		5.97
				tetrasilane		7.76
				$C_4Si_4H_{18}$		11.8
Molecular Sieve 13X	6	26	80	nitrogen	1'05"	
				carbon monoxide	2'12"	
			60	hydrogen	1'05"	
				nitrogen	1'54"	

TABLE II - I (cont'd)

		nitric oxide	2'36"
45	43	hydrogen	1'28"
	Ar	methane	3'14"

TABLE II - II

Materials Used

Material	Supplier	Purification
SiH_4	Merck, Sharpe and Dohme	Distilled at -160°C Degassed at -210°C
SiD_4	Merck, Sharpe and Dohme	Distilled at -160°C Degassed at -210°C
Si_2H_6	Merck, Sharpe and Dohme	Distilled at -126°C Degassed at -160°C
Si_2D_6	Merck, Sharpe and Dohme	Distilled at -126°C Degassed at -160°C
$C_6H_5SiD_3$	Merck, Sharpe and Dohme	Preparative G.L.C.
$C_6H_5SiD_3$	Laboratory preparation	Preparative G.L.C.
C_3H_8	Phillips	Distilled at -130°C Degassed at -160°C
C_3D_8	Merck, Sharpe and Dohme	Distilled at -130°C Degassed at -160°C
C_2H_4	Phillips	Degassed at 196°C
NO	Matheson	Passed through trap at -78°C, soda-lime trap and P_2O_5 column
N_2O	Matheson	Distilled at -130°C Degassed at -196°C
$1\text{-}C_4H_8$	Phillips	Research, 99.9+%
H_2	Airco	Assayed Reagent
D_2	Matheson	Passed through column of molecular sieves
$Hg(Me)_2$	Eastman Organic	Degassed at -95°C
He	Liquid Air	Passed through column of molecular sieves
Ar	Linde	Passed through column of molecular sieves

Procedure

Photolytic sources were allowed to warm up for at least one hour before use. For all quantitative runs the incident light intensity was measured before each run. All actinometry was done at ambient temperature. This meant if runs were performed at elevated temperatures the actinometric measurement was made the night before the actual experiment since the furnace was left to equilibriate overnight. Daily measurement of the light intensity was necessary because of the attenuation of the incident flux by the polymeric film deposited on the cell face during a run. Approximately one hour of irradiation was sufficient to reduce by one-half the total light absorbed in a freshly cleaned cell. At this point the cell was removed, and the polymer was washed off with dilute HF.

For compounds with significant vapour pressures the cell was filled by observing the pressure on the adjacent mercury manometer before closing the Hoke valve to the cell. For high pressure runs with low vapour pressure compounds the substrate was measured out in a known volume adjacent to the cell then the entire amount was frozen into the cell. In the cell all substrates, pure or mixtures, were allowed to diffuse for one hour at the cell temperature before irradiation. The time of irradiation was minimized to reduce secondary reactions. Substrate and products were frozen into a spiral trap at

liquid nitrogen temperature. Non-condensables were then pumped off through a U-trap also in liquid nitrogen and a solid nitrogen trap, by a single stage mercury diffusion pump to the Toepler and gas burette. Any monosilane, ethylene or nitric oxide present was trapped by the solid nitrogen. Appropriate slushes were used to separate the substrate from higher boiling compounds, always through the spiral and U-trap, and the substrate was saved for re-use. These higher boiling compounds were then subjected to g.c. analysis.

For phenylsilane the procedure had to be modified, only the non-condensables at -160°C were removed and the rest of the reaction mixture was injected into the g.c. In this case the reaction mixture was analyzed and the substrate was purified at the same time.

Additional Equipment

Mass spectral breakdown patterns were obtained from Associated Electronics Industries Model numbers MS2, MS9 and MS12.

Hydrogen isotope ratios were done on Associated Electronic Industries Model MS10.

Infra-red spectra were recorded on a Perkin-Elmer 421 spectrometer.

Nuclear Magnetic Resonance Spectra were obtained from a Varian 100 Mc machine.

Ultraviolet spectra and extinction coefficients were resolved on a Cary Model 14 spectrometer.

CHAPTER III

The $Hg(6\,^3P_1)$ Sensitized Decomposition of Disilane and Disilane-d_6, and the Reactions of Methyl Radicals and Hydrogen Atoms with Disilane

RESULTS

The mercury sensitization of disilane was studied as a function of substrate pressure, time, temperature, and added free radical scavengers in order to determine the nature of the processes responsible for the observed products: hydrogen, monosilane, trisilane, tetrasilane and a transparent polymeric film deposited on the cell face.

Additional information on the mechanism was gained from the products formed when methyl radicals or hydrogen atoms reacted with disilane. Both of these systems were studied as a function of disilane pressure and temperature.

The results reported here were obtained at room temperature unless otherwise noted.

1. The effect of substrate pressure on the sensitization of disilane.

The effect of substrate pressure on the product quantum yields was determined using short irradiation times. The results are given in Table III-I and Figure

TABLE III - I

Quantum Yield of Products as a Function of Pressure for the Photosensitization of Disilane-d_6 [(a)]

Disilane Pressure torr	I_a, μEinsteins/min		Φ, Moles/Einstein			
	before	after	D_2	SiD_4	Si_3D_8	Si_4D_{10}
11	0.151	0.140	0.32	0.36	0.049	0.099
30	0.187	0.151	0.44	0.53	0.096	0.247
96	0.139	0.132	0.55	0.58	0.039	0.38
125	0.193	0.170	0.52	0.64	0.069	0.39
148	0.235	0.209	-	-	0.045	0.36
155	0.209	0.187	0.52	0.61	0.059	0.39
170	0.132	0.125	0.46	0.52	0.055	0.40
170	0.237	0.221	0.65	0.77	0.074	0.38
170	0.221	0.194	0.56	0.81	0.085	0.44
200	0.172	0.182	0.47	0.50	0.067	0.41
200	0.182	0.166	0.54	0.65	0.072	0.48
300	0.238	0.226	0.56	0.58	-	-
300	0.226	0.200	0.54	0.66	0.071	0.057
300	0.200	0.172	0.54	0.62	0.072	0.56

(a) Photolysis time = 10 minutes.

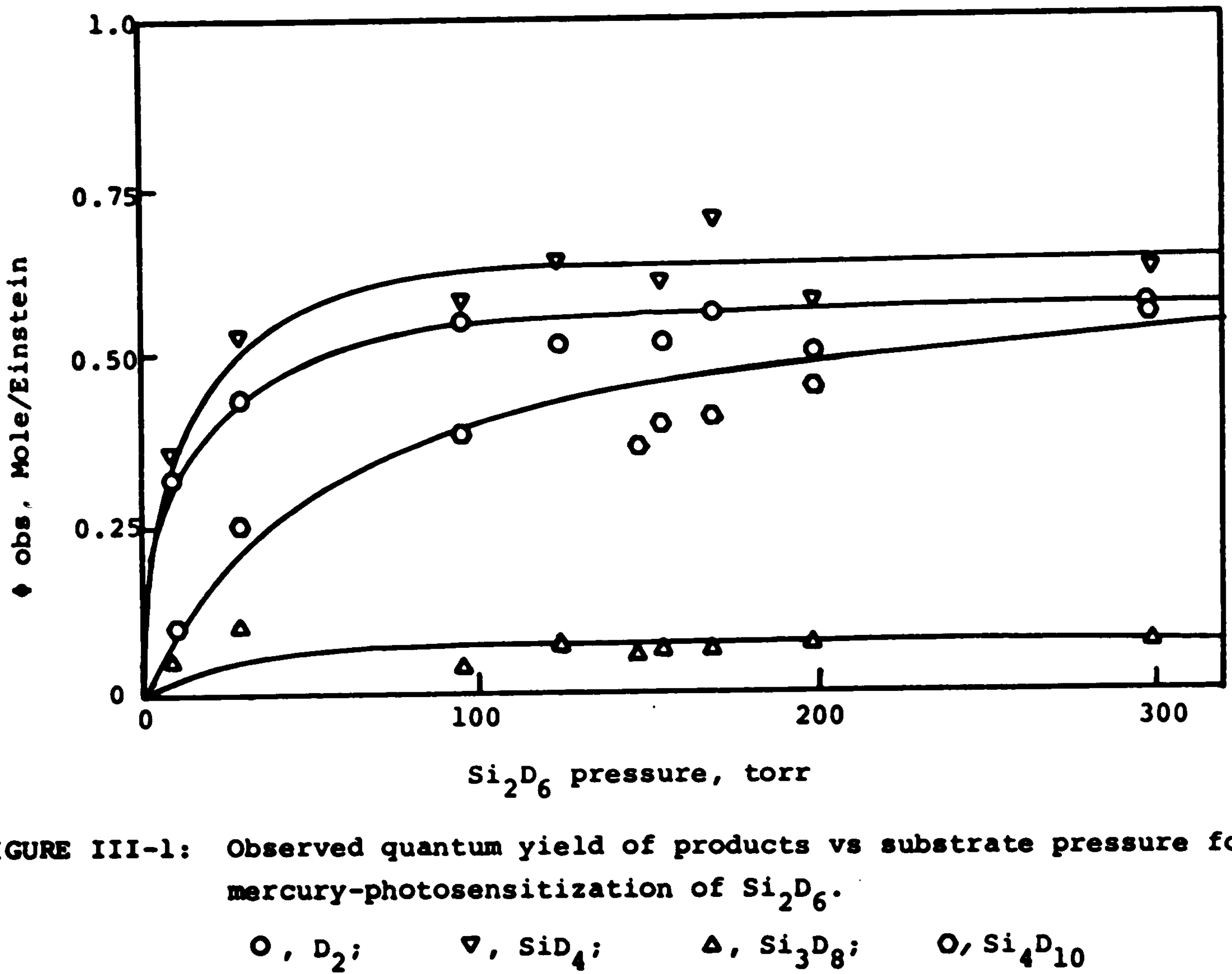


FIGURE III-1: Observed quantum yield of products vs substrate pressure for mercury-photosensitization of Si_2D_6.

O, D_2; ▽, SiD_4; △, Si_3D_8; O, Si_4D_{10}

III-1 for Si_2D_6 and Table III-II and Figure III-2 for Si_2H_6. The quantum yields for monosilane and hydrogen increase to plateau values above 100 torr but for tetrasilane considerably higher pressures are required. The quantum yield of trisilane varies little with pressure.

Only at the lowest measured pressure does the monosilane to hydrogen ratio change indicating that secondary decomposition of another product is contributing to the yield of one or both of them. The invariance of the quantum yields of the other products in their plateau region shows that the deficiency in the tetrasilane yield below 400 torr does not appear as a volatile product but probably contributes to polymer formation. The fall-off in all of the quantum yields below 50 torr is most probably caused by incomplete quenching.

The reported difference in quantum yields for the Si_2D_6 and Si_2H_6 systems is a function of the two different actinometers used to measure the absorbed light rather than a function of the substrate. This is obvious from the results when the two actinometric methods were used to obtain the quantum yield values in the H_2 + Si_2D_6 + Hg* system (vide infra), where the quantum yield of monosilane was 1.31 when 500 torr N_2O plus 1% 1-butene was used as the actinometer, but only 0.92 when 800 torr of propane containing the photostationary-state concentration of propylene was used. Clearly the actinometer

TABLE III - II

Quantum Yield of Products as a Function of Pressure for the Photosensitization of Disilane[a,b]

Disilane Pressure torr	I_a, μEinsteins/min		Φ, Moles/Einstein			
	before	after	H_2	SiH_4	Si_3H_8	Si_4H_{10}
10	0.215	0.183	0.50	0.45	-	-
27	0.183	0.157	0.58	0.74	0.059	0.21
51	0.157	0.148	0.65	1.03	0.048	0.31
101	0.148	0.135	0.70	0.85	0.068	0.47
200	0.135	0.130	0.71	0.79	0.13	0.57
402	0.130	0.128	0.76	0.87	0.11	0.73

(a) Photolysis time = 10 minutes

(b) Nitrous Oxide Actinometry

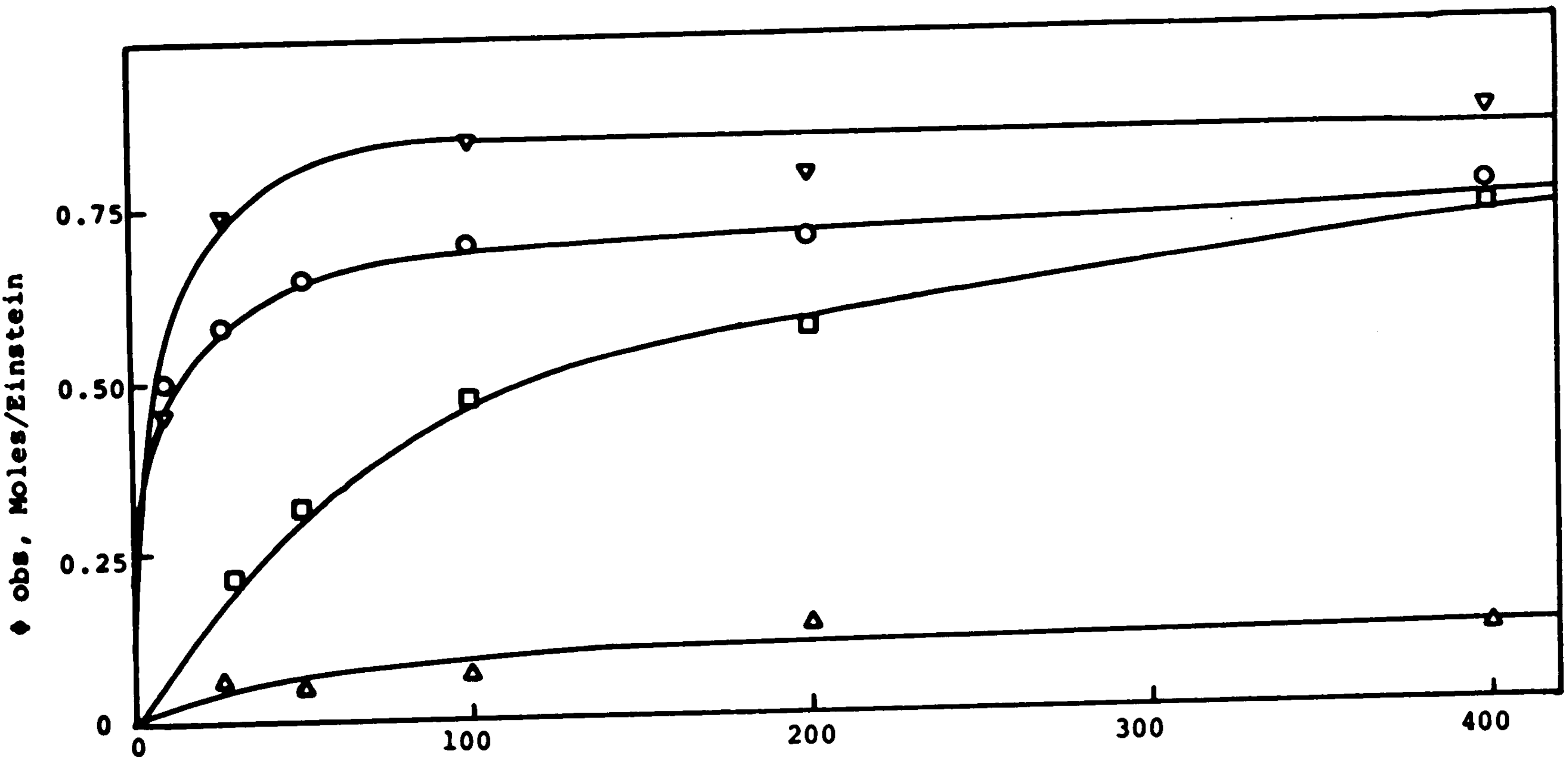


FIGURE III-2: Observed quantum yield of products vs substrate pressures for mercury photosensitization of Si_2H_6

○, H_2; ▽, SiH_4; △, Si_3H_8; □, Si_4H_{10}

interacts with the polymer deposited during a run and alters the transparency of the cell window. The two actinometric methods were compared in a clean cell (Appendix A) and the ratio of the measured light intensities was found to be $I_a(N_2O)/I_a(C_3H_8) = 1.00/0.85$. As a consequence, the quantum yields reported herein are based on a value of $\Phi_{H_2} = 0.58$ for the propane actinometer, rather than 0.50 unless otherwise annotated.

2. <u>The effect of exposure time on the product quantum yields.</u>

The effect of time on the product quantum yields was investigated at a disilane-d_6 pressure of 235 torr. The results, given in Table III-III and Figure III-3 show that all the products decline with increasing exposure time, the effect being greatest for the less stable trisilane and tetrasilane. The four products are all primary products since the extrapolated quantum yields at zero exposure time are: $\Phi(D_2) = 0.58$; $\Phi(SiD_4) = 0.73$; $\Phi(Si_3D_8) = 0.10$ and $\Phi(Si_4D_{10}) = 0.67$.

3. <u>Effect of the addition of the radical scavenger ethylene.</u>

By analogy with the methyl silanes the observed products could be formed from monoradicals and hydrogen atoms. On the other hand, disilane might resemble monosilane, in which case molecular eliminations could play

TABLE III - III

Quantum Yield of Products as a Function of Time for the Photosensitization of Disilane-d_6[(a)]

Time	I_a, μEinsteins/min		Φ, Moles/Einsteins			
Minutes	before	after	D_2	SiD_4	Si_3D_8	Si_4D_{10}
5	0.263	0.253	0.52	0.66	0.050	-
5	0.253	0.235	0.59	0.75	0.064	-
10	0.219	0.183	0.59	0.69	0.086	0.59
20	0.183	0.161	0.53	0.65	0.063	0.46
30	0.161	0.141	0.44	0.56	0.049	0.39
40	0.141	0.106	0.47	0.57	0.054	0.28

(a) Pressure 235 torr.

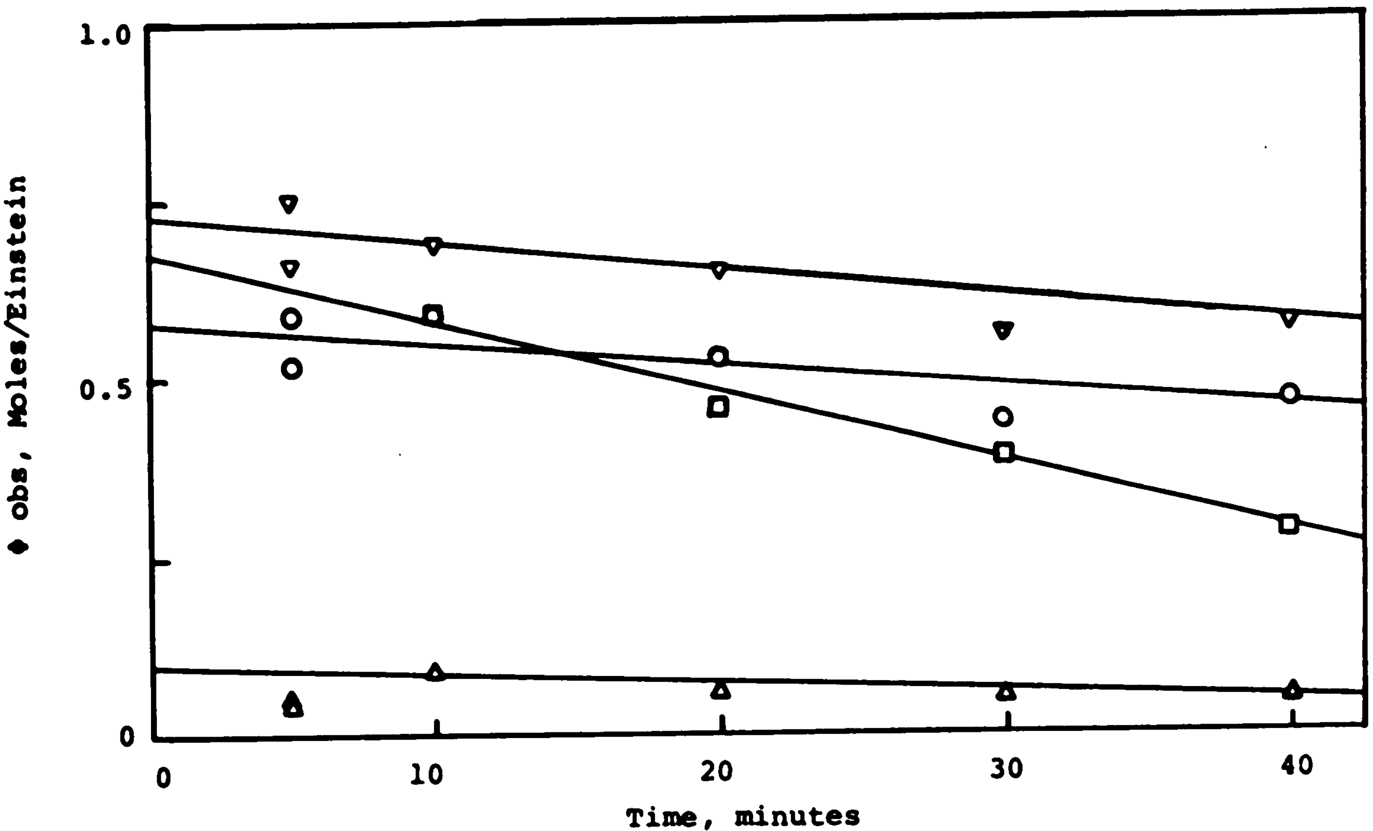


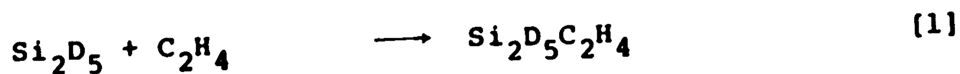
FIGURE III-3: Observed quantum yield vs exposure time for mercury photosensitization of 235 torr Si_2D_6.

○, D_2 ▽, SiD_4; △, Si_3D_8; □, Si_4D_{10}

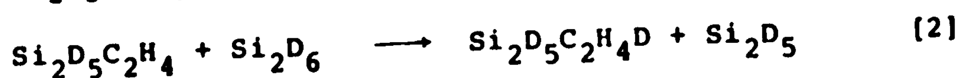
a significant role in the primary step. Ethylene was added as a radical trap. It has been shown to be an effective scavenger of monosilyl radicals (40) but unable to compete with a substrate silane for silylene radicals (18).

Table III-IV and Figure III-4 present the results from the addition of up to 4% ethylene to 200 torr of disilane-d_6. The tetrasilane-d_{10} yield was suppressed, monosilane was decreased by 28%, and deuterium and trisilane-d_8 remained unaffected. The major new product was ethyldisilane-d_6, and ethylsilane-d_4 was tentatively identified as a shoulder on the disilane-d_6 substrate peak by g.l.c.

The rapid decrease in the tetrasilane-d_{10} yield with added ethylene coupled with the rise of ethyldisilane-d_6 is indicative of the sequence,

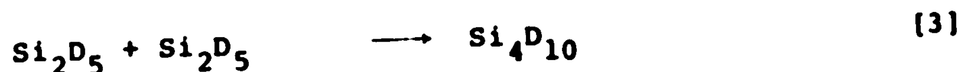


$$Si_2D_5 + C_2H_4 \longrightarrow Si_2D_5C_2H_4 \qquad [1]$$



$$Si_2D_5C_2H_4 + Si_2D_6 \longrightarrow Si_2D_5C_2H_4D + Si_2D_5 \qquad [2]$$

in which the precursors to tetrasilane-d_{10} are removed by addition to ethylene, i.e. step [1] occurs in place of step [3],



$$Si_2D_5 + Si_2D_5 \longrightarrow Si_4D_{10} \qquad [3]$$

The quantum yield of ethyldisilane-d_6 indicates that [1] and [2] are facile reactions even at room temperature. Similar reactions of the monosilyl-d_3 radical,

TABLE III - IV

Quantum Yield of Products as a Function of Added Ethylene for the Photosensitization of Disilane-d_6[(a)]

Ethylene Pressure torr	I_a µEinsteins/min	Φ, Moles/Einsteins				
		D_2	SiD_4	Si_3D_8	Si_4D_{10}	$C_2H_4Si_2D_5$
0	0.154	0.57	0.60	0.085	0.50	-
2.15	0.158	0.59	0.70	0.063	0.072	1.33
2.83	0.142	0.58	0.61	0.062	0.043	1.89
6.01	0.132	0.58	0.50	0.059	0.024	1.50
8.0	0.127	0.58	0.52	0.080	0.022	2.26

(a) 200 torr of disilane-d_6 and 15 minutes photolysis time.

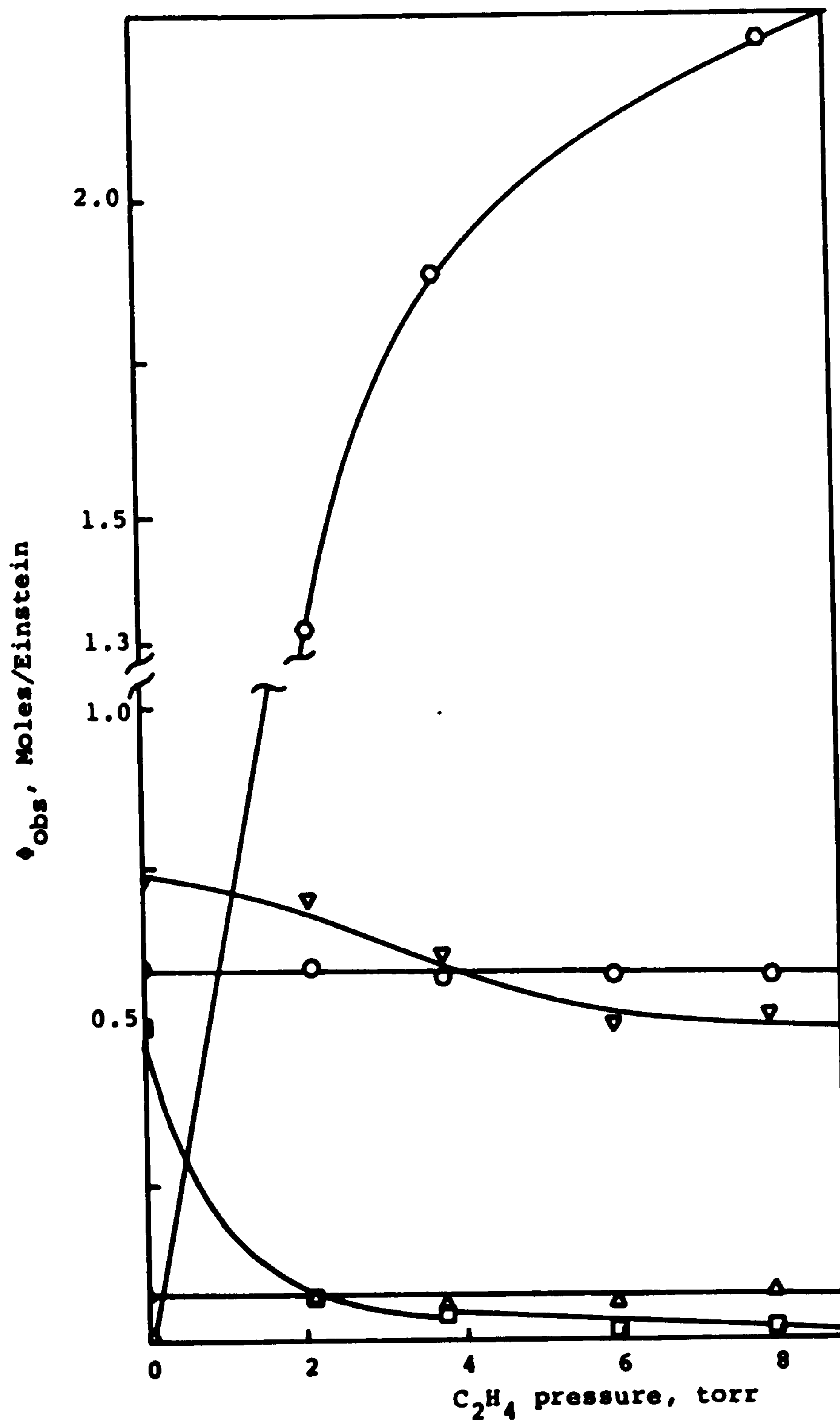
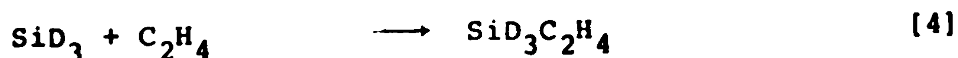
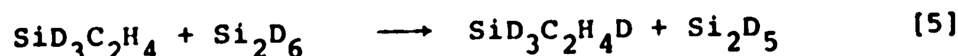


FIGURE III-4: Observed quantum yield vs C_2H_4 pressure for mercury photosensitization of 200 torr Si_2D_6.

O , D_2; ▽ , SiD_4; △ , Si_3D_8; □ , Si_4D_{10}; O , $C_2H_4Si_2D_6$



$$SiD_3 + C_2H_4 \longrightarrow SiD_3C_2H_4 \qquad [4]$$



$$SiD_3C_2H_4 + Si_2D_6 \longrightarrow SiD_3C_2H_4D + Si_2D_5 \qquad [5]$$

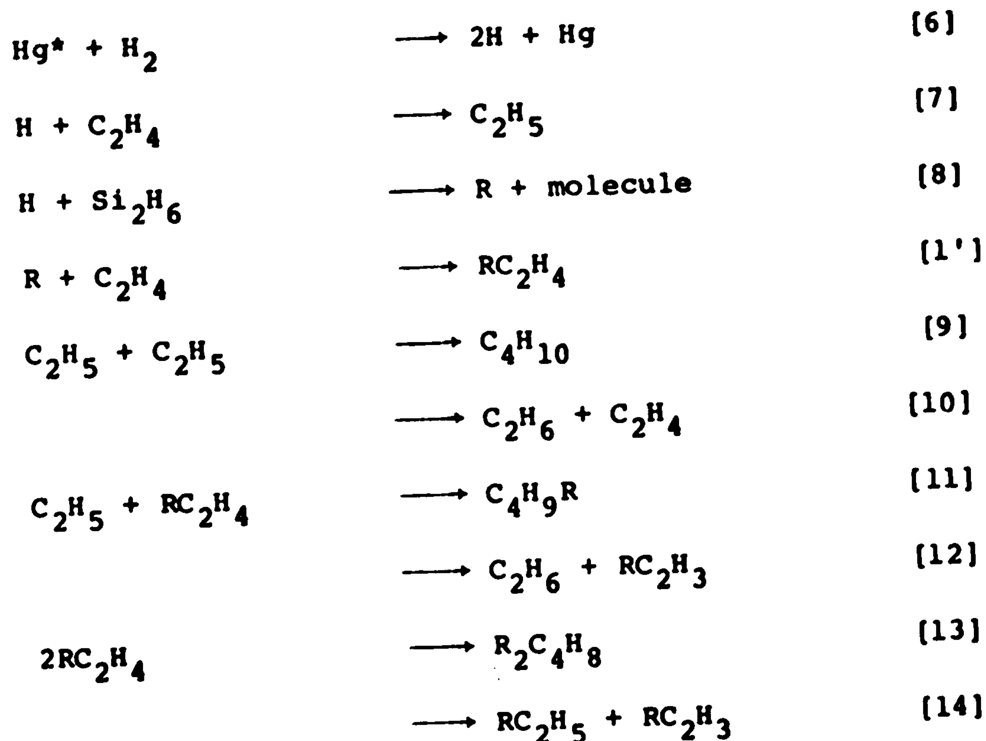
account for the qualitative observation of ethylsilane-d_4.

Deuterium and the unscavenged monosilane-d_4 now appeared to be molecular elimination products and the trisilane-d_8 could result from insertion of SiD_2 into a substrate molecule. Another possibility for the observed behaviour of the deuterium and monosilane-d_4 yield was that deuterium atoms reacted faster with substrate to produce deuterium and monosilane-d_4 than they did with the added ethylene. This is consistent with the known kinetics of the reaction between hydrogen atoms and monosilane (55,56).

Auxiliary competitive rate experiments were done to determine the rate of reaction of H atoms with disilane. Disilane and ethylene were allowed to compete for the hydrogen atoms formed by the mercury photosensitization of molecular hydrogen (Table III-V). The butane yield gave an accurate measure of the extent of the reaction in the absence of any competing species (127) and the decrease in the butane yield was a measure of the relative rates of reaction of hydrogen with ethylene and the competing molecule.

In this system the following scheme is applicable

$$Hg + h\nu \xrightarrow{\lambda = 253.7\ nm} Hg^* \qquad Ia$$



$$Hg^* + H_2 \longrightarrow 2H + Hg \quad [6]$$

$$H + C_2H_4 \longrightarrow C_2H_5 \quad [7]$$

$$H + Si_2H_6 \longrightarrow R + \text{molecule} \quad [8]$$

$$R + C_2H_4 \longrightarrow RC_2H_4 \quad [1']$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \quad [9]$$

$$\longrightarrow C_2H_6 + C_2H_4 \quad [10]$$

$$C_2H_5 + RC_2H_4 \longrightarrow C_4H_9R \quad [11]$$

$$\longrightarrow C_2H_6 + RC_2H_3 \quad [12]$$

$$2RC_2H_4 \longrightarrow R_2C_4H_8 \quad [13]$$

$$\longrightarrow RC_2H_5 + RC_2H_3 \quad [14]$$

where R represents a silyl radical. The silyl radicals are removed by addition to ethylene as was shown in Table III-IV. Ethyl radicals do not add to ethylene under the conditions of this experiment (127), and the rate constant for this addition is $10^{6.6}$ cc/mole-sec (128,129). This is about the same value as that measured for the abstraction of a hydrogen atom from disilane by simple alkyl radicals, $10^{7.1}$ cc/mole-sec (86). Radical-radical reactions, therefore, were the sole mode of removal of C_2H_5 and RC_2H_4. The following approximations can then be made,

$$2K = 2(k_9 + k_{10}) = (k_{11} + k_{12}) = 2(k_{13} + k_{14}).$$

This simplifies the expression for steady-state radical concentrations to

$$Ia = K([Si_2H_5] + [RC_2H_4])^2$$

The following relation can then be derived,

$$\frac{Rate°(C_4H_{10})}{Rate\ (C_4H_{10})} = (1 + \frac{k_8[Si_2H_6]}{k_7[C_2H_4]})^2 \qquad (a)$$

where Rate°(C_4H_{10}) is the rate of formation of n-butane when no competing gas is present and Rate(C_4H_{10}) is the rate of formation of n-butane in the mixture. The ratio k_8/k_7 derived from the slope of the lines in Figure III-5 is 3.2 for disilane and 1.7 for disilane-d_6. Hydrogen atoms reacted with disilanes faster than they added to an equal concentration of ethylene at room temperature, and certainly are a possible source of "unscavengable" hydrogen and monosilane.

It was concluded that disilanyl radicals added readily to the olefin and that the disilanyl radicals gave rise to tetrasilane; monosilyl radicals were not the sole precursors to the monosilane product; hydrogen atoms, if present would not be scavenged by ethylene; and the intermediates which produce trisilane were not completely removed by ethylene.

4. Effect of the addition of nitric oxide.

Small concentrations of nitric oxide suppress

TABLE III - V

Butane Yield from the Reaction of Hydrogen Atoms with Ethylene in the Presence of Disilane

Time Minutes	I_a μEinsteins/min	Pressure of Reactant: H_2	Pressure of Reactant: Disilane torr	Pressure of Reactant: C_2H_4	Product: $n\text{-}C_4H_{10}$ μmoles	$\frac{\text{Rate }(C_4H_{10})^{\circ}}{\text{Rate }(C_4H_{10})}$
		Disilane = Si_2H_6				
11	0.23	470	2.15	2.84	0.19	11.6
10	0.23	400	2.37	5.35	0.36	5.50
10	0.23	400	2.70	9.78	0.56	3.54
		Disilane = Si_2D_6				
11	0.23	403	2.47	6.08	0.76	2.93
10	0.23	420	2.44	10.12	0.92	2.20
10	0.23	410	2.30	9.6	1.38	1.47

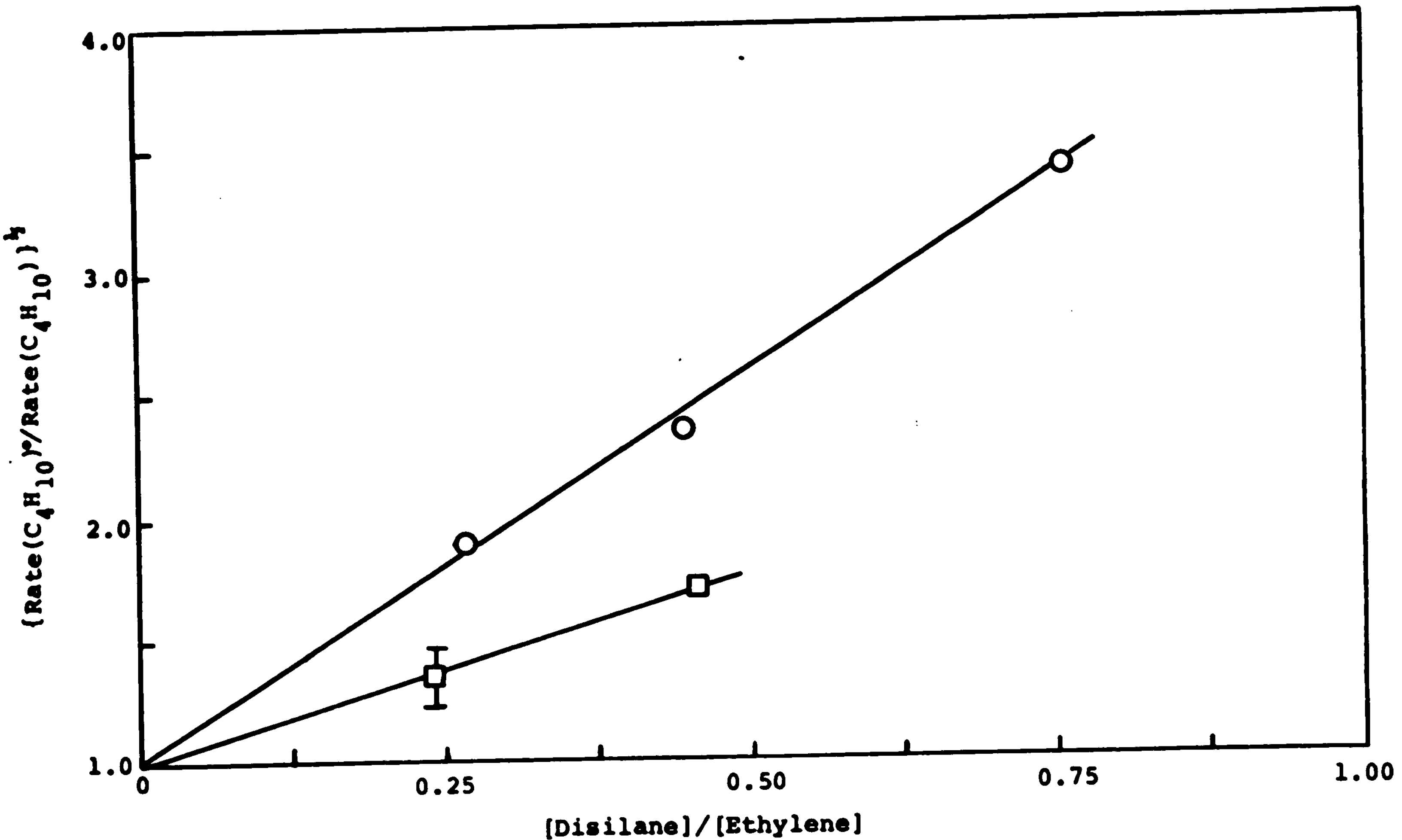


FIGURE III-5: Plot of equation (a) from data in Table III-V. ○, Si_2H_6; □, Si_2D_6

the dimerization of silyl and methyl-substituted silyl monoradicals (56) but do not remove silylene radicals (60,61). Addition of nitric oxide to the disilane system should then complement the ethylene scavenging study. The results are given in Table XI. Broadly speaking, the effect on the product silanes was the same as it was for ethylene: tetrasilane was practically suppressed, monosilane was not completely eliminated and trisilane was again largely unaffected. In addition the hydrogen yield was increased and nitrogen and nitrous oxide were formed. Four new products were eluted on the g.l.c.; one between disilane and trisilane and three between trisilane and tetrasilane. Mass analysis of these compounds utilizing a g.l.c. leak into a rapid scan mass spectrometer showed them to be oxygen containing silanes. Deuterium substitution on the disilane and $N^{15}O$ were used to aid in the identification, in no instance were the ions found to contain nitrogen. Tentative assignments of the structures are given in Table III-VI under A, B, C and D, in their order elution from the g.l.c. column. The mass spectra can be found in Appendix B along with that of a fifth compound E, which was eluted from the column into the mass spectrometer before A, but was not resolved on the thermal conductivity detector.

The yield of oxygen containing silanes was computed by assuming that the sensitivity of the detector

TABLE III - VI

Photosensitization of Si_2H_6 in the Presence of NO[a]

Si_2H_6 Pressure torr	NO Pressure torr	Products (μmole)									
		H_2	N_2	N_2O	SiH_4	Si_3H_8	Si_4H_{10}	A $SiH_3OSi_2H_5$	B $SiH_3O(SiH_2O)_3SiH_3$	C $(SiH_2O)_4$ (cyclic)	D $(Si_2H_5)_2O$
200	0	1.37	0	0	1.14	0.033	1.01	0	0	0	0
200	2	(b)	(b)	(b)	(b)	0.040	0.165	(a)	(a)	(a)	(a)
200	2.5	1.77	2.68	2.90	0.70	0.014	0.020	0.592	0.016	0.223	0.212
200	4	2.54	3.08	2.08	0.56	0.033	0.031	1.05	0.062	0.313	0.175
200	5	3.1	3.3	2.6	0.63	(b)	(b)	(b)	(b)	(b)	(b)
200	6	3.23	3.67	2.32	0.62	0.023	0.031	0.601	0.219	0.624	0.098
175	10.0	(b)	(b)	(b)	0.46	(b)	(b)	(b)	(b)	(b)	(b)
175	16.6	(b)	(b)	(b)	0.44	(b)	(b)	(b)	(b)	(b)	(b)

(a) Photolysis time 10 minutes

(b) Not determined

was the same for the four silicon atom skeleton as for tetrasilane, and that a similar relation was valid between trisilane and the oxygen containing three silicon atom skeleton. The results showed a deficit in the oxygen atom material balance.

Mention should be made of the fact that nitric oxide served to eliminate the deposition of polymer on the cell wall as evidenced by the absence of any attenuation of the light intensity during runs with nitric oxide, in fact the amount of light absorbed by the actinic compound was greater after a run than before, in a used cell (Table III-VII).

A further observation was that the peak area ratios changed with time when the condensable products were allowed to stand at room temperature (Table III-VIII). For this reason the product analyses reported in Table III-VI were always done immediately after separation of the products from the substrate by low temperature distillation. The more highly-oxygenated compounds E, B and C were formed at the expense of the siloxanes A and D(Table III-VIII), which fact, coupled with the material imbalance for oxygen suggested that there is an uncharacterized highly oxygenated intermediate of limited stability at room temperature responsible for the observed behaviour.

The products indicated the presence of monosilyl

TABLE III - VII

The Effect of Nitric Oxide on the Rate of Formation of Hydrogen and the Absorbed Light Intensity in Consecutive Runs

Run #	Time Min.	Si_2H_6 Pressure torr	NO Pressure torr	$d[H_2]/dt$ μmoles/min	I_a μEinsteins/min
249	10	200	0	0.204	
250	10	200	0	0.164	
251	10	200	0	-	
252	10	200	0	0.127	
253	10	200	5	-	
254	10	200	5	-	
255	10	200	5	-	
256	12	200	2	-	
257	11	200	0	0.137	
2-95	10	383	23.6		0.115
2-96	11	175	10.0		0.122
2-99	11	174	16.6		0.128

TABLE III - VIII

Peak Area Ratios as a Function of Time at Room Temperature for Condensable Products from Si_2H_6:NO = 200:5

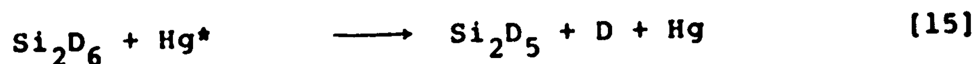
Photolysis time 30 minutes

Time Minutes	$\frac{Si_3H_8O}{Si_3H_8O_2}$ $(\frac{A}{E})$	$\frac{Si_3H_8}{Si_3H_8O_2}$	$\frac{Si_4H_{10}O_3}{Si_3H_8O_2}$ $(\frac{B}{E})$	$\frac{(Si_4H_8O_4)}{Si_3H_8O_2}$ $(\frac{C}{E})$	$\frac{(Si_2H_5)_2O}{Si_3H_8O_2}$ $(\frac{D}{E})$
0	2.91	0.253	0.099	0.38	0.354
90	1.61	0.028	0.111	0.24	0.097

and disilanyl radicals since $SiH_3OSi_2H_5$ and $Si_2H_5OSi_2H_5$ were both formed. As in the ethylene scavenging, the monosilane could not be completely eliminated. The unscavengable monosilane and the trisilane must then arise from intermediates which were not removed by nitric oxide, such as H atoms, silylenes, or from a molecular process.

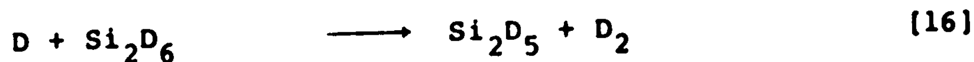
5. Isotopic labelling experiments.

The scavenging studies established that disilanyl and monosilyl radicals were formed in the mercury sensitization of disilane. By analogy with the mercury sensitization of the methyl silanes a probable mode of formation of disilanyl radicals was by scission of a silicon-deuterium bond in the primary step,



$$Si_2D_6 + Hg^* \longrightarrow Si_2D_5 + D + Hg \qquad [15]$$

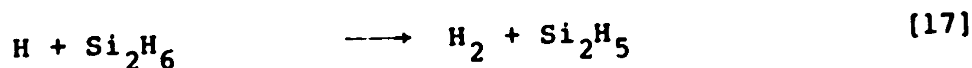
followed by the abstraction reaction,



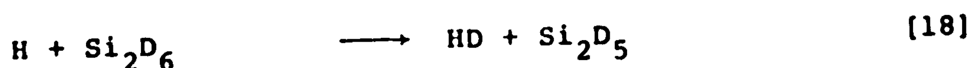
$$D + Si_2D_6 \longrightarrow Si_2D_5 + D_2 \qquad [16]$$

to give another disilanyl radical. The importance of steps [15] and [16] was tested by sensitizing an equimolar mixture of 300 torr of disilane and disilane-d_6 and analyzing the hydrogen fraction for its isotopic content. The distribution of H_2:HD:D_2 was 2.4:2.7:1.0 demonstrating that H atoms and D atoms were indeed present in the system and that there existed a significant k_H/k_D kinetic

isotope effect for the abstraction reactions of hydrogen atoms:



$$H + Si_2H_6 \longrightarrow H_2 + Si_2H_5 \quad [17]$$



$$H + Si_2D_6 \longrightarrow HD + Si_2D_5 \quad [18]$$

Isotopic analysis of the monosilane fraction from the equimolar mixture ruled out any major contribution from molecular elimination of monosilane in a primary step since the SiD_3H concentration was greater than the SiD_4 concentration (Table B-VIII, Appendix B).

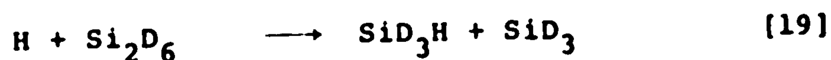
The mass spectrum of the tetrasilane fraction is included in Table B-IX, Appendix A, along with the spectra for Si_4H_{10} and Si_4D_{10}, (Table B-III, Appendix B) for comparison. Table B-IX shows no m/e ratio greater than the ion corresponding to $Si_2H_5Si_2D_5^+$ and indicates that Si_2H_5 must be the dominant disilanyl radical in the system: this confirms the existence of significant isotope effect for the abstractions by the hydrogen and deuterium atoms.

It was concluded that primary step [15] was operative with a minimum efficiency of 0.6 as given by the quantum yield of D_2; that the atoms produced in primary step [15] exhibited an isotope effect in their abstraction reactions with Si_2H_6 and Si_2D_6; that the major mode of formation of monosilane was via some reaction other than molecular elimination in a primary step; and that disilanyl radicals recombined to give tetrasilane.

6. The reactions of H atoms with disilane-d_6.

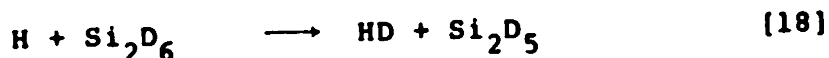
Hydrogen atoms were produced by the mercury photosensitization of molecular hydrogen in the presence of disilane-d_6. The results, given in Table III-IX and Figure III-6, showed monosilane to be the major product with lesser amounts of trisilane and tetrasilane. Isotopic analysis of the monosilane showed the presence of both SiD_4 and SiD_3H (Table B-10, Appendix B). Monosilane does not give a parent ion, but the observed relative intensities of SiD_3^+ and SiD_2H^+ were nearly equal. Neglecting isotope effects, the concentration of SiD_3H in the mixture was a minimum of 50% of the total monosilane; if the cracking reaction exhibited a H/D isotope effect the SiD_3H fraction would be greater.

These observations dictated a displacement type reaction between hydrogen atoms and the disilane molecule,



$$H + Si_2D_6 \longrightarrow SiD_3H + SiD_3 \qquad [19]$$

in addition to the more common abstraction type reaction of hydrogen atoms,



$$H + Si_2D_6 \longrightarrow HD + Si_2D_5 \qquad [18]$$

Since the quantum yield of hydrogen atom production in the mercury photosensitization of H_2 is two, the rate constant ratio k_{18}/k_{19} can be estimated to be 1.2, if it is assumed that the difference 2-Φ(monosilane) correctly

TABLE III - IX

Quantum Yield of Products from the Photosensitization of Hydrogen with Added Disilane-d_6 [a]

Disilane Pressure torr	I_a µEinsteins/min before	I_a µEinsteins/min after	H_2 / Si_2D_6	Φ, Moles/Einstein Monosilane	Φ, Moles/Einstein Trisilane	Φ, Moles/Einstein Tetrasilane
2.25	0.30	0.24	256	-	0.17	0.080
2.07	0.25	0.21	222	0.77	0.18	0.073
3.54	0.24	0.20	113	0.80	0.19	0.11
5.28	0.19	0.15	89	0.81	-	-
5.45	0.27	0.24	103	0.92	0.22	0.14
6.95	0.21	0.19	85	0.87	0.19	0.14
10.29	0.19	0.16	90	0.91	0.19	0.19
19.36	0.16	0.16	67	0.90	0.14	0.22

(a) Photolysis time = 10 minutes

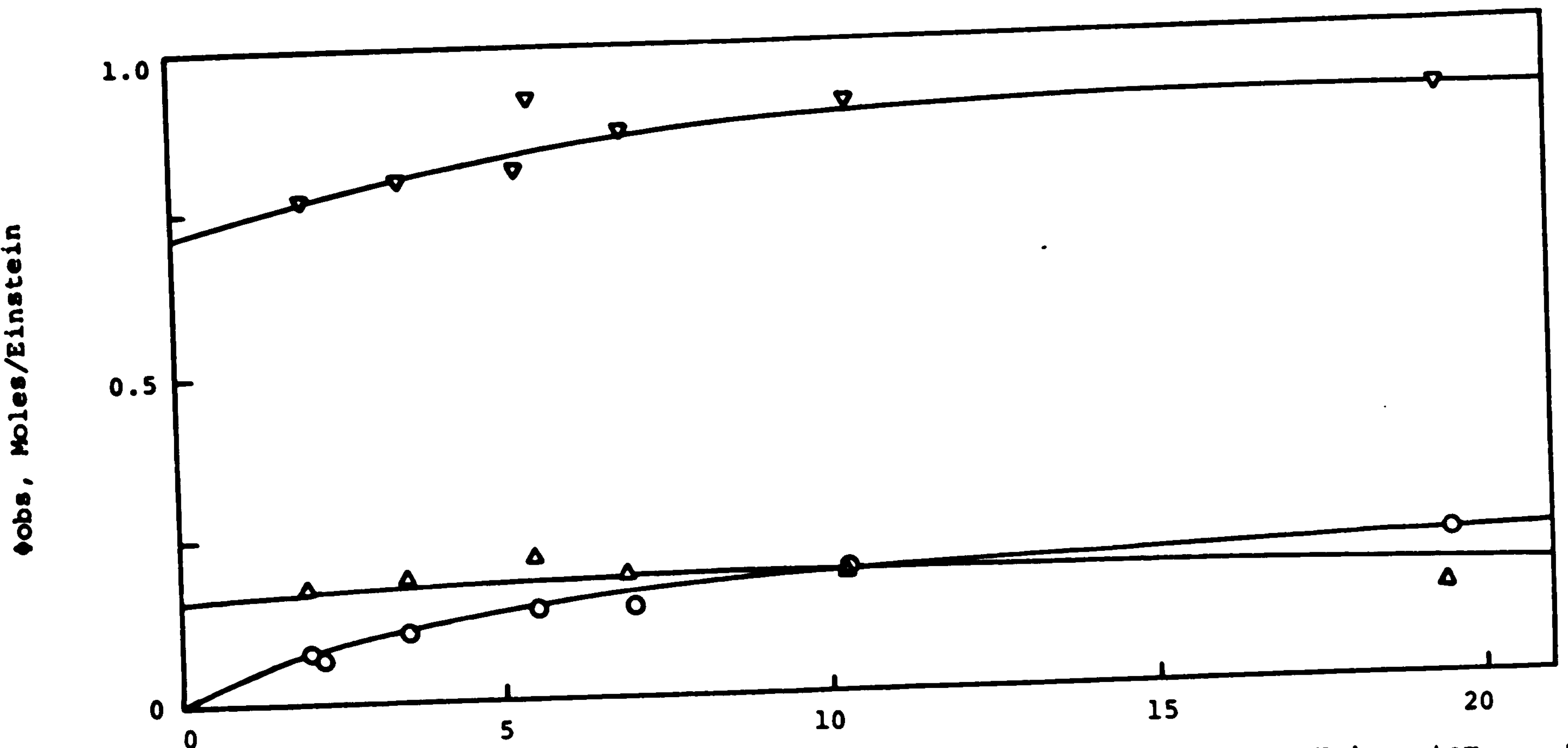
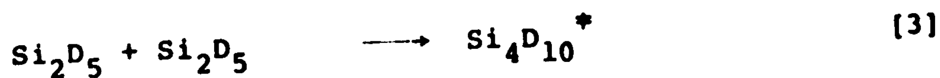


FIGURE III-6: Observed quantum yield vs Si_2D_6 pressure for H_2 + Si_2D_6 + Hg* system H_2:Si_2D_6 = 100:1.

▽, monosilane; △, trisilane; O, tetrasilane.

represents the quantum yield for step [19]. This provides a mechanism for formation of monosilane which cannot be completely suppressed by low concentrations of either ethylene or nitric oxide and points to a single primary step in the mercury photosensitization, silicon-hydrogen bond cleavage.

The low quantum yield of tetrasilane, 0.2, even in the presence of one atmosphere of hydrogen suggested that hydrogen might be a poor moderator for the vibrationally excited tetrasilane formed by the dimerization of disilanyl radicals,



$$Si_2D_5 + Si_2D_5 \longrightarrow Si_4D_{10}^{*} \qquad [3]$$

$$Si_4D_{10}^{*} \longrightarrow \text{fragmentation} \qquad [20]$$

$$\xrightarrow{M} Si_4D_{10} \qquad [21]$$

When deuterated propane was added as a moderator, Table III-X, the product yields were not appreciably influenced. It was concluded that the observed dependence of the tetrasilane yield on disilane pressure was due to a reaction between a radical intermediate and a disilane molecule rather than a third body requirement for the combination of disilanyl radicals.

The system was also used to look at the recombination of monosilyl radicals. Hydrogen was mercury-sensitized together with an equimolar mixture of

TABLE III - X

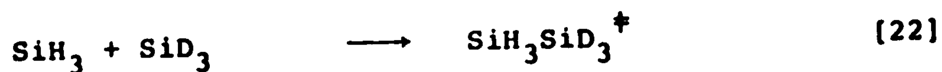
Photosensitization of H_2 with Added Si_2D_6 = 15 torr in the Presence of C_3D_8 [(a)]

H_2 Pressure torr	C_3D_8 Pressure torr	PRODUCTS (μmoles)		
		Monosilane	Trisilane	Tetrasilane
1250	0	1.70	0.31	0.37
1250	50	1.69	0.43	0.42
1200	100	1.66	0.38	0.38
1200	150	(b)	0.27	0.24
1250	150	(b)	0.29	0.30
870	200	1.69	0.30	0.24

(a) Photolysis time = 10 minutes

(b) Not determined

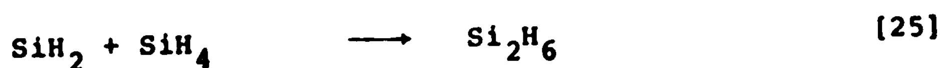
SiH_4 and SiD_4. Disilane was produced with a quantum yield of 0.30 and the isotopic composition of the disilane was determined by mass spectrometry utilizing the cracking patterns published by Ring et al. (63). The distribution of the hydrogen isotopes in the disilane (Table B-XI, Appendix B) indicated that most of the disilane came from insertion of a silylene into either SiD_4 or SiH_4, rather than from combination of two silyl radicals. A probable sequence of reactions for the labelled radicals is:



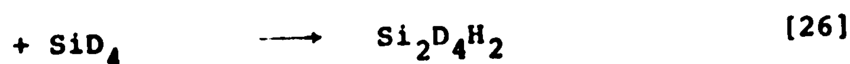
$$SiH_3 + SiD_3 \longrightarrow SiH_3SiD_3^{\ddagger} \quad [22]$$

$$SiH_3SiD_3^{\ddagger} \longrightarrow SiH_3D + SiD_2 \quad [23]$$

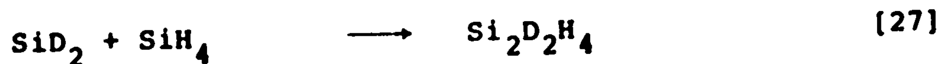
$$\longrightarrow SiD_3H + SiH_2 \quad [24]$$



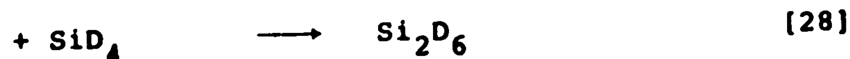
$$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \quad [25]$$



$$+ SiD_4 \longrightarrow Si_2D_4H_2 \quad [26]$$



$$SiD_2 + SiH_4 \longrightarrow Si_2D_2H_4 \quad [27]$$



$$+ SiD_4 \longrightarrow Si_2D_6 \quad [28]$$

This accounts for the observed absence of SiH_3SiD_3 among the products. The vibrationally excited disilane molecule formed in reaction [22] decomposes before it can be stabilized by the 400 torr of hydrogen present in the reaction cell. The silylenes formed in [23] and [24] then give rise to disilanes with only even numbers of deuterium and protium atoms in reactions [25] - [28].

7. <u>The reactions of methyl radicals with disilane</u>.

Both the mercury sensitization of, and the reactions of hydrogen atoms with, disilane gave monosilyl radicals as well as disilanyl radicals. In an effort to obtain a unique source of disilanyl radicals mercury dimethyl was photolyzed in the presence of varying amounts of disilane and the results are presented in Table III-XI. The reaction turned out to be more complex than anticipated; in addition to the products listed in Table III-XI thirteen other minor peaks were eluted from the g.l.c. column. Mass spectra of these peaks indicated that they were multimethylated silanes. It is significant that neither methylsilane nor tetrasilane was a major product of the reaction. This means that at room temperature the displacement type reaction

$$CH_3 + Si_2D_6 \longrightarrow CH_3SiD_3 + SiD_3 \qquad [29]$$

could not be important and that some reaction other than self-combination was removing the disilanyl radicals. It was also observed that the ethane yield was lower than would be expected. When methane is formed only by abstraction from disilane by the methyl radical, the ratio of the rate of abstraction to the square root of the rate of self-combination is given by

$$\frac{R_{CH_3D}}{R_{C_2H_6}^{\frac{1}{2}}} = \frac{k_{abstraction}[Si_2D_6]}{k^{\frac{1}{2}}_{combination}}$$

TABLE III - XI

Photolysis of $(CH_3)_2Hg$ in the Presence of Si_2D_6 at Room Temperature[(a)]

Si_2D_6 Pressure torr	$(CH_3)_2Hg$ Pressure torr	PRODUCTS						
		CH_4 μmoles	$\frac{CH_4}{\Sigma CH_3}$	$\frac{C_2H_6}{\Sigma CH_3}$	$\frac{CH_3SiD_3}{\Sigma CH_3}$	$\frac{SiD_4}{\Sigma CH_3}$	$\frac{Si_3D_8}{\Sigma CH_3}$	$\frac{Si_4D_{10}}{\Sigma CH_3}$
10.5	9	1.35	.282	.334	0.050	0.011	0.018	0.007
49	9.2	5.42	.641	.160	0.039	0.141	0.018	0.011
49.5	9	3.50	.586	.174	0.065	0.023	0.023	0.020
99	9	9.55	.830	.075	0.021	0.035	0.016	0.022
101	9.0	9.75	.794	.088	0.030	0.031	0.010	0.016
101	3.0	10.4	.985	.003	0.010	0.031	0.021	0.005
102	9	10.0	.841	.068	0.023	0.038	0.008	0.009
125	9.0	11.2	.927	.030	0.013	0.026	0.012	0.004
125	9.0	10.9	.949	.021	0.009	0.020	0.010	0.006
125	9	15.6	.958	.015	0.013	0.019	0.004	0.005
140	9	11.4	.746	.092	0.070	0.028	0.010	0.016

(a) Photolysis Time = 15 minutes

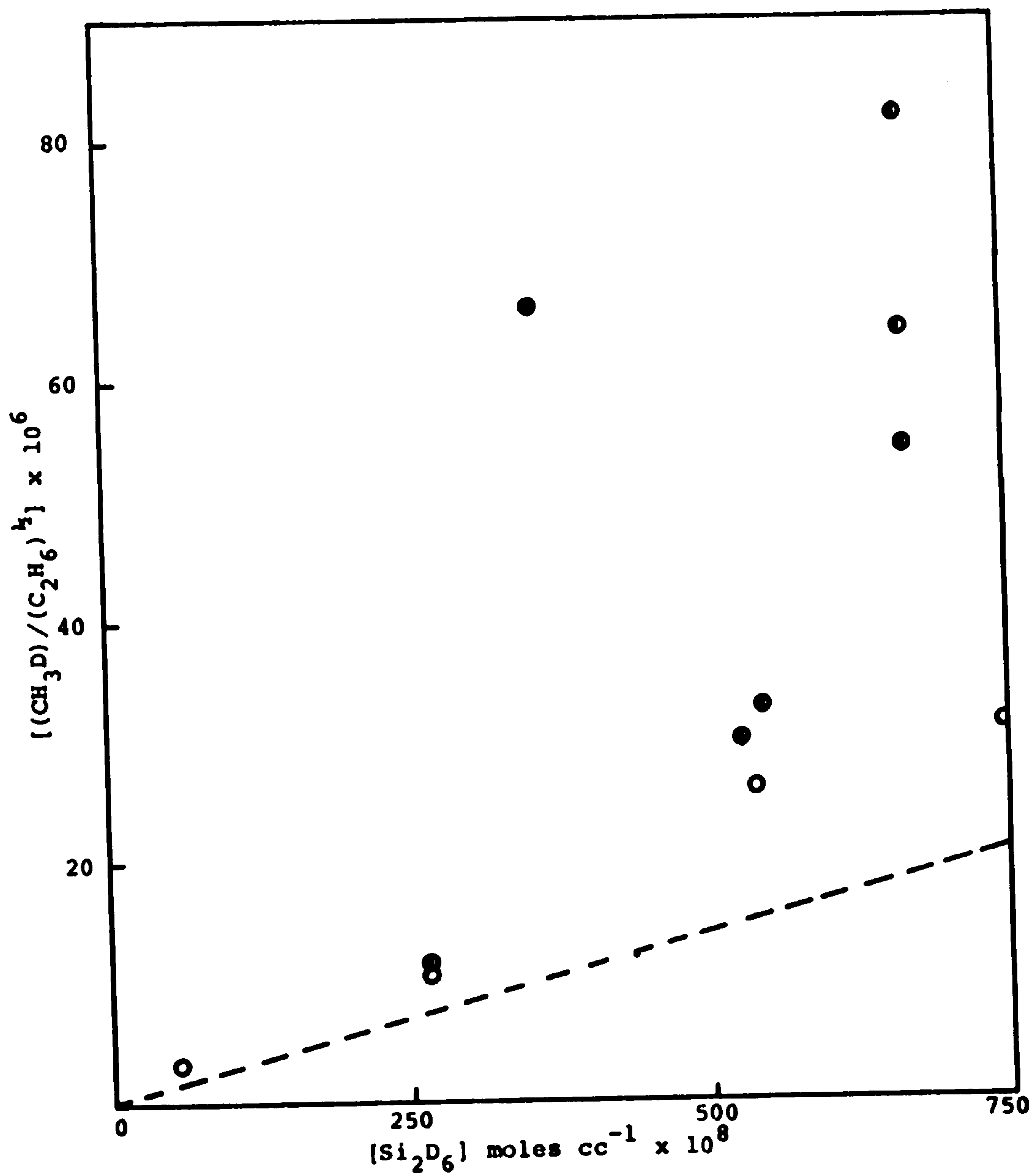


FIGURE III-7: $CH_3 + Si_2D_6$ at room temperature.

O, clean cell; ●, used cell; --- calculated slope

This is a function linear in substrate concentration and deviations from linearity indicate additional modes of formation of methane. The appropriate plot is made in Figure III-7 where the dotted line is the slope calculated from the published rate constants, the open circles are for runs done in an unused cell and the half-filled circles represent runs carried out in a used cell. The value in brackets is the number of previous runs done in the same cell. Obviously other processes are contributing to the formation of methane and the extent of this contribution is dependent on the previous history of the reaction vessel. In view of the low yield of tetrasilane a likely process is the disproportionation of methyl radicals with disilanyl radicals [31], in competition with the abstraction reaction [30],

$$CH_3 + Si_2D_6 \longrightarrow CH_3D + Si_2D_5 \quad [30]$$

$$CH_3 + Si_2D_5 \longrightarrow CH_3D + Si_2D_4 \quad [31]$$

$$CH_3 + Si_2D_4 \longrightarrow CH_3D + Si_2D_3, \text{ etc.} \quad [32]$$

This system was not a unique source of disilanyl radicals.

8. The effect of temperature on the quantum yields in the systems $Hg^* + Si_2H_6$, $CH_3 + Si_2D_6$ and $H + Si_2D_6$.

All three systems were studied over a range from room temperature to ∿220°C. Blank runs established

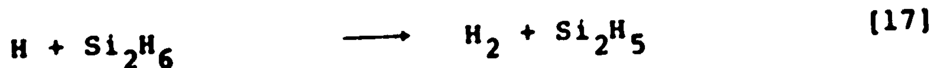
that thermal decomposition of substrate was not occurring. Trisilane is reported to undergo no measurable decomposition below 300°C (45-47), so thermolysis of products during the fifteen minute photolysis runs was not a complicating factor.

The quantum yields for the Hg* + Si_2H_6 system are reported in Table III-XII. It is seen that the results fall into two broad categories. Below 150°C the hydrogen and tetrasilane yields were relatively constant, while the trisilane and monosilane yields had a slightly positive temperature coefficient. Above 150°C on the other hand, all the products increased with increasing temperature and the mono- and trisilane became the major products. This is graphically illustrated in Figures III-8 and III-9 where log (Φ) is plotted vs. 1/T. The two regions appear as straight lines with a break in the slope corresponding to ~150°C.

In the region below 150°C where temperature had a minimum effect on the hydrogen quantum yield, the postulated primary step is independent of temperature,

$$Hg^* + Si_2H_6 \longrightarrow H + Si_2H_5 + Hg \qquad [33]$$

The fragments further react as follows,



$$H + Si_2H_6 \longrightarrow H_2 + Si_2H_5 \qquad [17]$$

$$\longrightarrow SiH_4 + SiH_3 \qquad [34]$$

TABLE III - XII

Quantum Yield of Products as a Function of Temperature for the Photosensitization of 400 torr of Disilane[(a)]

Temperature °C	I_a µEinsteins/min before	I_a µEinsteins/min after	Φ, Moles/Einstein H_2	SiH_4	Si_3H_8	Si_4H_{10}
25	0.281	0.287	0.56	0.56	0.07	0.42
25	0.123	0.124	0.66	0.66	0.14	0.41
26	0.280	0.250	0.72	0.66	0.015	0.67
65	0.129	0.123	0.68	0.73	0.36	0.46
67	0.117	0.117	0.71	0.71	-	-
67	0.144	0.101	0.62	0.69	0.14	0.37
108	0.155	0.155	0.64	1.16	0.19	0.44
122	0.250	0.197	0.84	1.05	0.19	0.65
143	0.197	0.134	0.87	1.58	-	-
157	0.164	0.155	0.69	1.75	1.05	0.54
160	0.166	0.164	0.69	1.86	0.96	0.53
161	0.287	0.254	0.70	1.48	0.82	0.59
173	0.134	0.100	1.16	2.78	1.13	0.66
191	0.100	0.071	1.23	3.68	1.84	0.71
212	0.155	0.129	1.83	7.04	3.68	0.90

(a) Photolysis time = 10 minutes

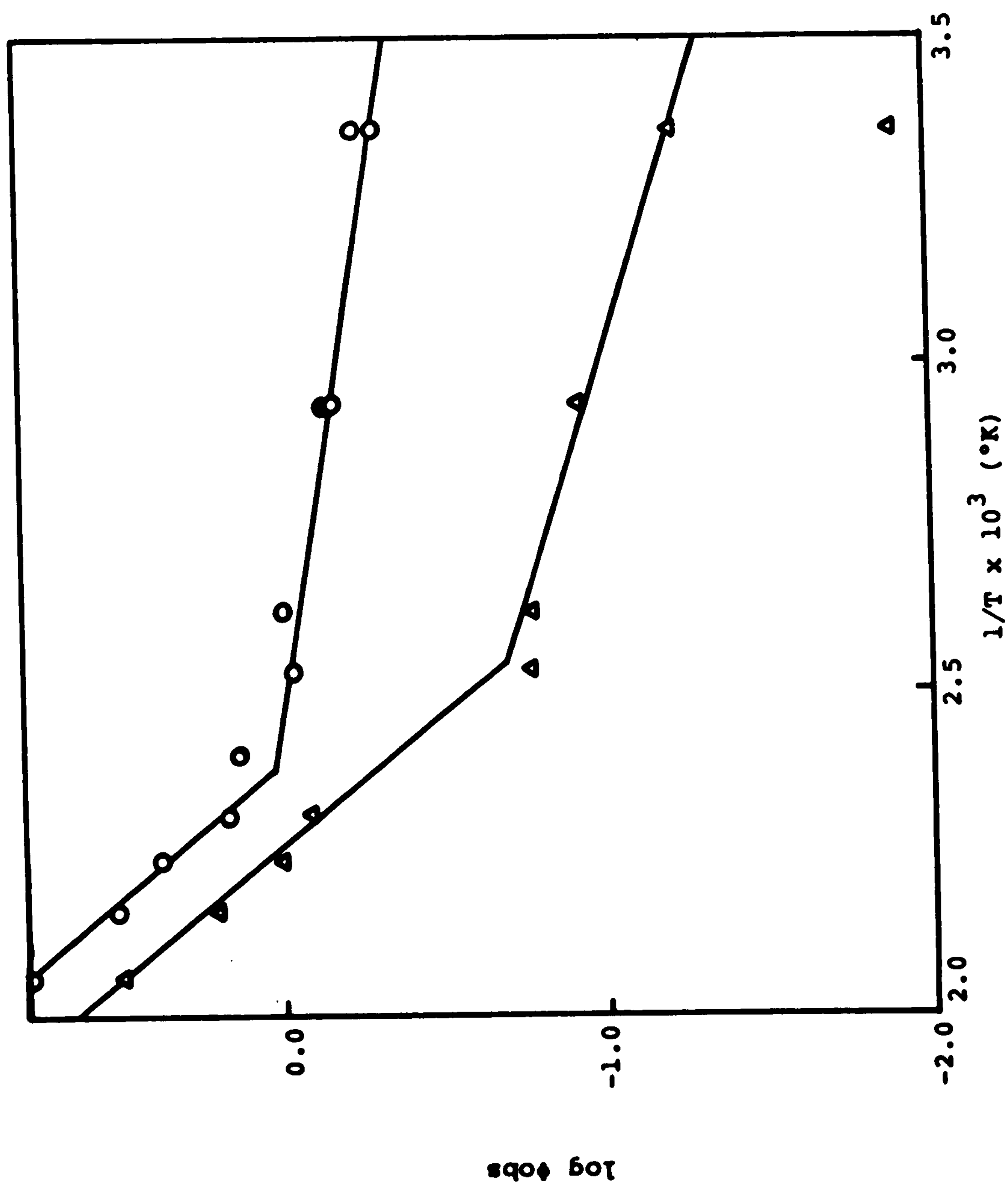


FIGURE III-8: Arrhenius plot of Hg* + Si_2H_6 system.

O, monosilane; Δ, trisilane.

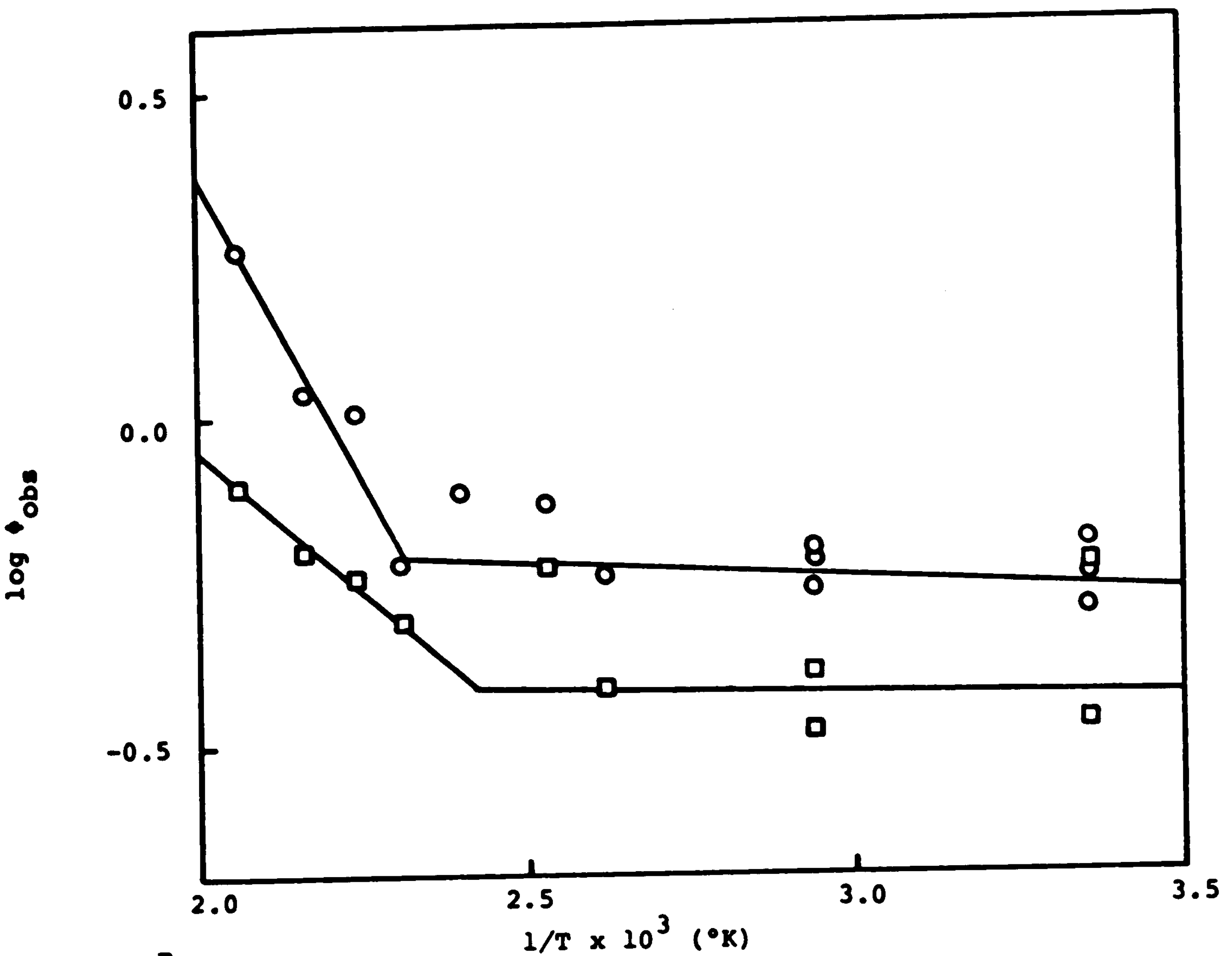
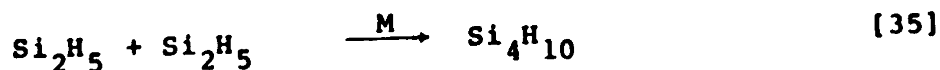


FIGURE III-9: Arrhenius plot of Hg* + Si_2H_6 system.

O , hydrogen; □ , tetrasilane.



$$Si_2H_5 + Si_2H_5 \xrightarrow{M} Si_4H_{10} \qquad [35]$$

Steps [17] and [34], abstraction reactions, are expected to be temperature dependent whereas [35], a radical-radical combination, is not. The expression for the hydrogen quantum yield is

$$\Phi_{H_2} = \frac{k_{17}}{k_{17} + k_{34}}$$

which can be rearranged to

$$\frac{1}{\Phi H_2} - 1 = \frac{k_{34}}{k_{17}}$$

The log of the L.H.S. of this equation is plotted versus the reciprocal of the absolute temperature in Figure III-10. From the slope of the line and the intercept the Arrhenius parameters for k_{17} and k_{34} are calculated to be,

$$\log(A_{17}/A_{34}) = 0.61 \pm 0.15$$

$$E_{17} - E_{34} = 0.50 \pm 0.24 \text{ kcal/mole.}$$

The monosilane formed directly in step [34] will show very little variation with temperature thus this reaction is not responsible for the observed positive dependence.

Since part of the monosilane can be scavenged, the monosilyl radicals must react further to form monosilane. Reactions which must be considered are,

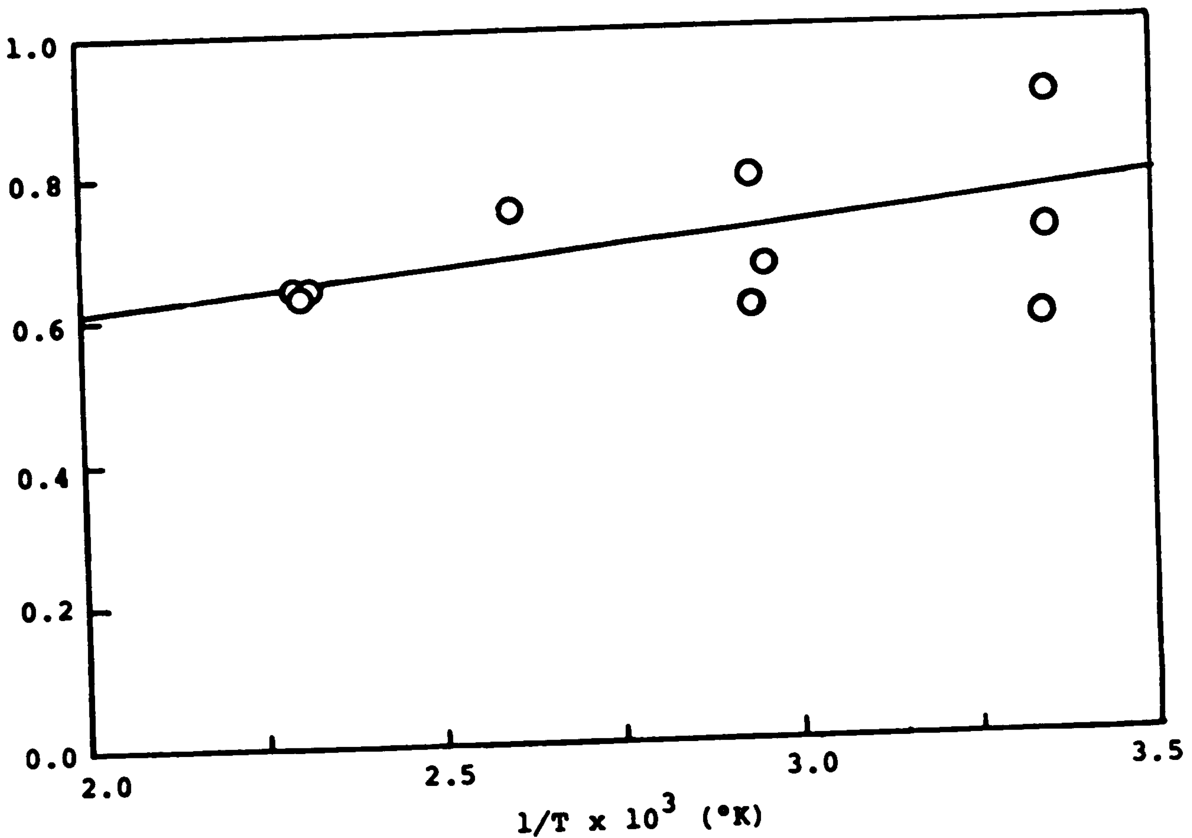
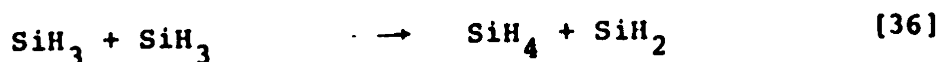
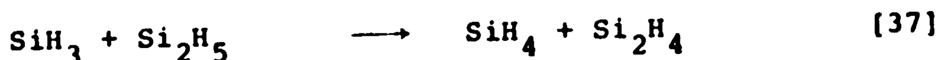


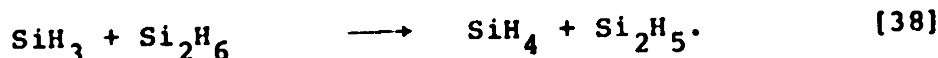
FIGURE III-10: A plot of log $(1/\Phi_{H_2} - 1)$ vs 1/T for the Hg* + 400 torr of Si_2H_6 system.



$$SiH_3 + SiH_3 \longrightarrow SiH_4 + SiH_2 \quad [36]$$



$$SiH_3 + Si_2H_5 \longrightarrow SiH_4 + Si_2H_4 \quad [37]$$

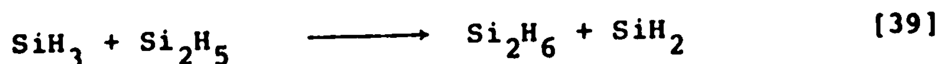


$$SiH_3 + Si_2H_6 \longrightarrow SiH_4 + Si_2H_5\cdot \quad [38]$$

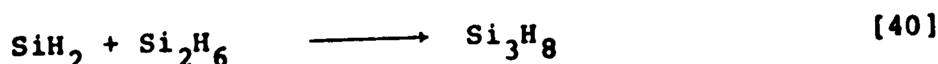
Steps [36] and [37] are then the most probable monosilane forming steps at room temperature, if the abstraction reaction [38] has an activation energy of 10-12 kcal/mole as is the case for the analogous hydrocarbon reactions. As the temperature is increased the contribution from step [38] will become important, thus making it responsible for the observed positive temperature coefficient.

Evidence so far has indicated that trisilane is unscavengable, thus it could come from elimination of silylene which then inserts into disilane. It was observed however, that methyl radicals tended to disproportionate with disilanyl radicals to give methane plus a diradical. The unscavengable nature of trisilane may then arise from the silylene formed when the nonsilyl radicals present in the scavenging systems disproportionate with a silyl radical to terminate the chain. If this is the case the trisilane yield would indeed remain largely unaffected in the presence of radical scavengers. The positive temperature coefficient would then result from an activation energy associated with the insertion reaction.

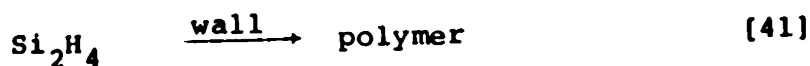
The steps which might be considered in this temperature interval include [17], [33-38] plus the following,



$$SiH_3 + Si_2H_5 \longrightarrow Si_2H_6 + SiH_2 \quad [39]$$



$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \quad [40]$$



$$Si_2H_4 \xrightarrow{wall} polymer \quad [41]$$

$$SiH_2 \xrightarrow{wall} polymer \quad [42]$$

Step [39] is the disproportionation which complements [37]; [40] produces the "unscavengable" trisilane and, [41] and [42] are the polymer-forming steps.

At temperatures above 150°C this sequence of reactions cannot account for the observed products. Additional reactions, which break the silicon-silicon bond and generate hydrogen atoms, are required. A change in the primary step such as,

$$Hg^* + Si_2H_6 \longrightarrow 2H + Si_2H_4 + Hg$$

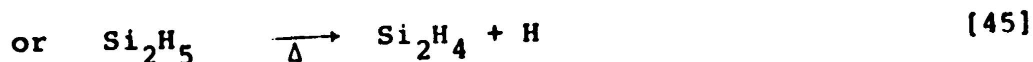
or

$$\longrightarrow SiH_3 + SiH_3$$

is not adequate; the products are formed in some chain mechanism. The most probable process is one in which an intermediate decomposes to give fragments which will produce the products and regenerate itself such as,

$$Si_2H_5 \xrightarrow[\Delta]{} SiH_2 + SiH_3 \qquad [43]$$

and $$SiH_3 \xrightarrow[\Delta]{} SiH_2 + H \qquad [44]$$



or $$Si_2H_5 \xrightarrow[\Delta]{} Si_2H_4 + H \qquad [45]$$

No one of these steps can explain the observed increase in all of the products. If a suitable source of one of the intermediates could be found it might be possible to differentiate among the processes giving rise to the various products.

Methyl radicals plus disilane would be a source of disilanyl at higher temperatures where the abstraction reaction would predominate over the disproportionations found to be operative at room temperature. A temperature study of this system would provide information on the thermal stability of the disilanyl radical. The results from such a study are tabulated in Table III-XIII. As before methyl silane-d_3 was not a major product of this reaction which indicates that methyl radicals exclusively abstract in their reactions with disilane-d_6. Trisilane-d_8 and monosilane-d_4 were the major products at higher temperatures, thus Si_2D_5 radicals can give rise to products containing an odd number of silicon atoms. The Si_3D_8 and SiD_4 differed by approximately the same amount excluding the room temperature run. When this is taken into consideration the two odd-numbered silicon products

TABLE III - XIII

Photolysis of $(CH_3)_2Hg$ in the Presence of Si_2D_6 as a Function of Temperature for Photolysis Time of 15 Minutes

Si_2D_6 Pressure torr	$(CH_3)_2Hg$ Pressure torr	Temp. °C	CH_3D μmoles	$\frac{CH_3D}{\Sigma CH_3}$ (a)	$\frac{C_2H_6}{\Sigma CH_3}$	$\frac{CH_3SiD_3}{\Sigma CH_3}$	$\frac{SiD_4}{\Sigma CH_3}$	$\frac{Si_3D_8}{\Sigma CH_3}$	$\frac{Si_4D_{10}}{\Sigma CH_3}$
140	9	25	11.3	0.746	0.092	0.070	0.028	0.009	0.016
142	2.5	89	16.9	1.0	0	0.007	0.154	-	-
142	2.0	89	11.3	1.0	0	0.007	0.168	0.021	0.098
159	2.2	89	12.2	1.0	0	0.007	0.156	0.020	0.090
147	1.46	116	7.0	1.0	0	0.007	0.228	0.045	0.112
147	1.8	167	8.1	1.0	0	0.007	0.272	0.100	0.148
147	1.8	217	7.4	1.0	0	0.007	0.612	0.444	0.226
152	1.7	217	6.3	1.0	0	0.007	0.520	0.488	0.244

(a) $\Sigma CH_3 = [CH_3D] + 2[C_2H_6] + [CH_3SiD_3]$.

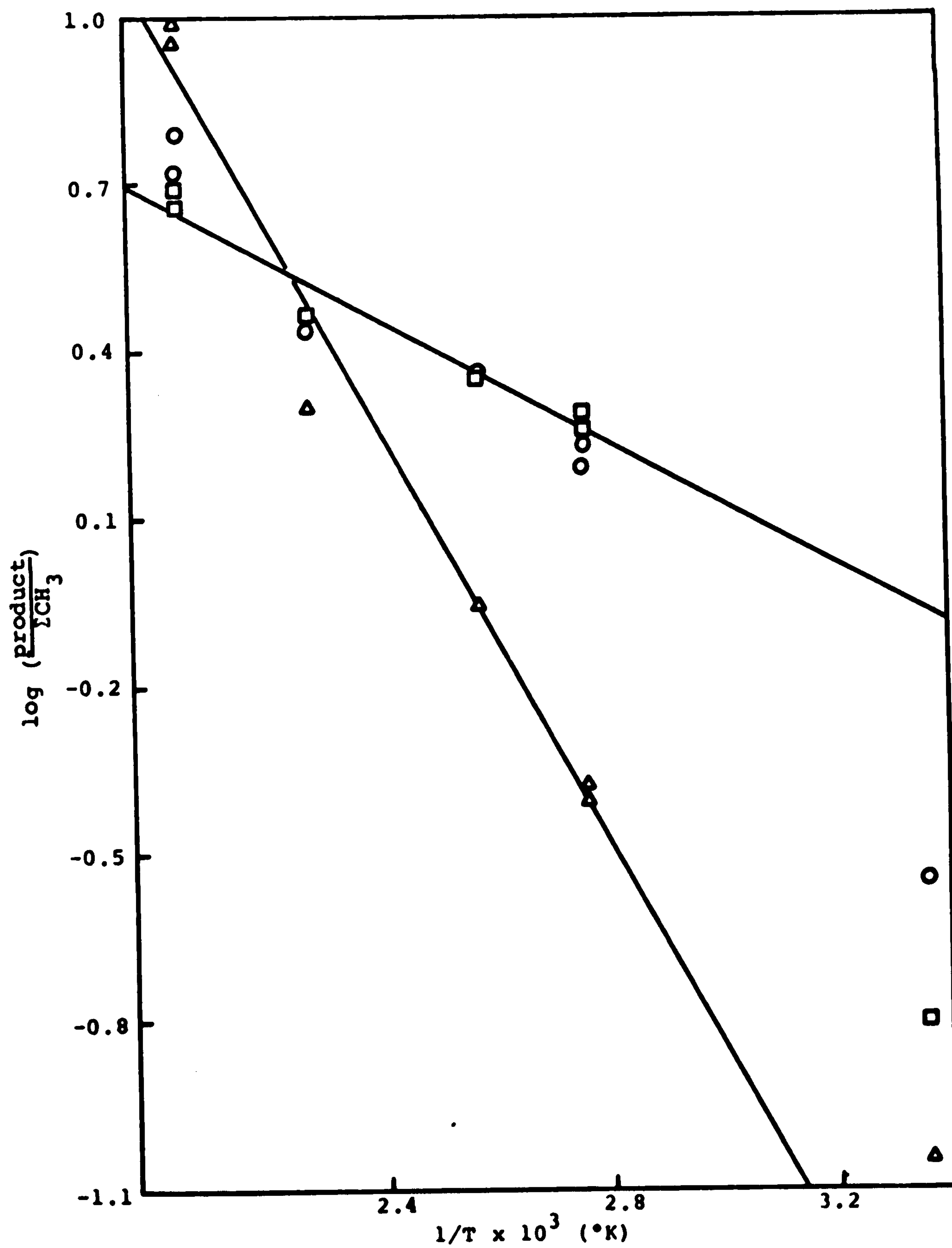
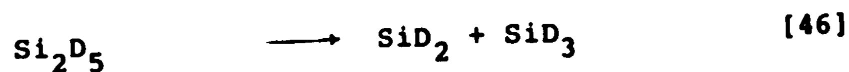


FIGURE III-11: Arrhenius plot of $(CH_3)_2Hg + Si_2D_6$ system.

O, SiD_4; Δ, Si_3D_8; □, Si_4D_{10}

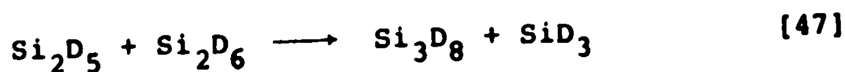
exhibit the same temperature dependence. Arrhenius type plots are made from the data in Table III-XIII in Figure III-11 and from the slopes for the Si_3D_8 and Si_4D_{10} the apparent energies of activation are 8.4±0.5 and 2.5±0.2 kcal/mole, respectively.

The mass balance between SiD_4 and Si_3D_8 suggested that reaction [46]



$$Si_2D_5 \longrightarrow SiD_2 + SiD_3 \qquad [46]$$

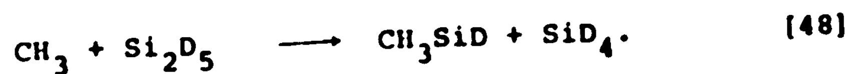
might be responsible for the two products but the low apparent activation energy argued against a unimolecular scission of the silicon-silicon bond. It is more probably a bimolecular reaction such as



$$Si_2D_5 + Si_2D_6 \longrightarrow Si_3D_8 + SiD_3 \qquad [47]$$

which gave rise to the observed concentrations of mono- and trisilane.

The almost constant difference between SiD_4 and Si_3D_8 is not inconsistent with a mechanism in which the methyl radicals generated in the photolytic step undergo a disproportionation with Si_2D_5 to give methyl silylene plus monosilane,



$$CH_3 + Si_2D_5 \longrightarrow CH_3SiD + SiD_4. \qquad [48]$$

Deuterium was not a product of this system. This ruled out step [45] as a source of hydrogen atoms in

the mercury sensitization case. It also militated against reaction [44], loss of hydrogen from monosilyl, since SiD_3 radicals were almost certainly present in the methyl plus disilane-d_6 system.

A further check was made by looking at the effect of temperature on the H atom plus disilane-d_6 system. Any change in the quantum yield of hydrogen would not be noticed in this system nor would it be possible to see any increase in the other products caused by a chain mechanism because of the low concentration of disilane. However, decomposition of either SiD_3 or Si_2D_5 radicals would manifest itself as a decrease in the observed quantum yields. The results are displayed in Table III-XIV and Figure III-12. The monosilane yield was not significantly altered. The Si_3D_8 and Si_4D_{10} both decreased. This corroborates the evidence from the methyl plus disilane system that the monosilyl radical does not decompose. The decrease in Si_3D_8 reflects the decrease in SiD_2 caused by the tendency for monosilyl radicals to abstract rather than disproportionate at higher temperatures.

At least part of the decrease in observed quantum yields is due to the actinometric method used. The cell was not allowed to cool to room temperature before the actinometric determinations were made. A

TABLE III - XIV

Quantum Yield of Products from Photosensitization of Hydrogen in the Presence of Disilane-d_6 as a Function of Temperature[a,b]

Temp. °C	I_a µEinsteins/min before	I_a µEinsteins/min after	Φ, Moles/Einstein Monosilane	Trisilane	Tetrasilane
25	0.091	0.085	1.35	0.28	0.19
60	0.108	0.091	1.24	0.16	0.16
116	0.128	0.108	1.37	0.08	0.16
168	0.201	0.128	1.26	0.06	0.14
215	0.274	0.201	1.29	0.09	0.10

(a) Nitrous oxide actinometry

(b) Pressure H_2 = 400 torr; Si_2D_6 = 6.0 torr; Photolysis time = 10 min.

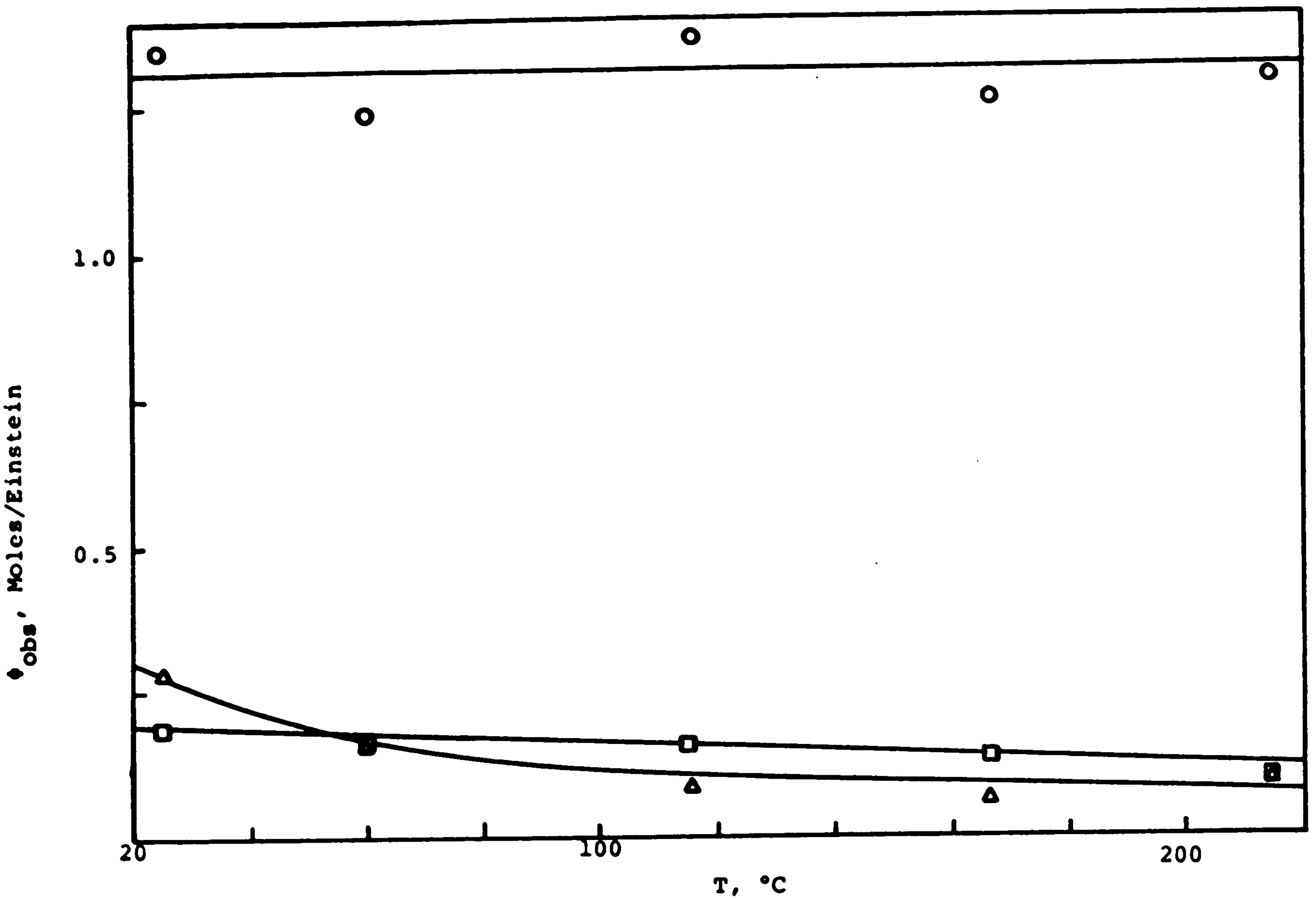


FIGURE III-12: Observed quantum yield of products vs temperature for $H_2 + Si_2D_6 + Hg^*$ system.

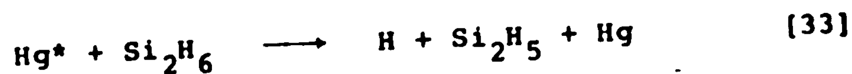
O , monosilane; △ , trisilane; □ , tetrasilane

subsequent check showed that the quantum yields at 215°C were 20% low but this did not fully account for the observed decrease. Some decomposition of disilyl might be occurring under the experimental conditions, most likely by silicon-deuterium bond scission.

DISCUSSION

1. Formation of the Monoradicals.

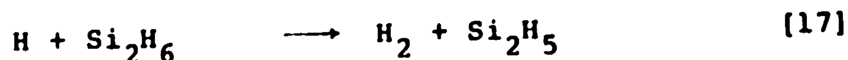
The results indicate that hydrogen atoms and disilanyl radicals were the sole products of the primary quenching act in the mercury photosensitization of disilane:



$$Hg^{*} + Si_2H_6 \longrightarrow H + Si_2H_5 + Hg \qquad [33]$$

This is similar to the single hydrogen loss in the primary cleavage found for paraffins and methyl-substituted silanes but in contrast to the results for monosilane where loss of more than one hydrogen occurred in the primary step (56). It is also significant in that energy transfer must be associated more with the hydridic hydrogen atom than with the large more polarizable silicon atom, since the quenching cross-section data available indicate that the silicon-silicon linkage is a very effective quencher of excited mercury atoms (Table I-III). The results further indicate that the hydrogen atoms from reaction [33] either abstract a

hydrogen atom from the substrate,



$$H + Si_2H_6 \longrightarrow H_2 + Si_2H_5 \qquad [17]$$

or displace a silyl radical from disilane,

$$H + Si_2H_6 \longrightarrow SiH_4 + SiH_3 \qquad [34]$$

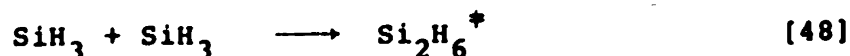
Subsequent reactions of the silyl radicals are responsible for the observed product distributions.

2. Reactions of the Monoradicals.

a) Combinations and Disproportionation

The self and cross combinations of the two radicals will be considered. Each of these reactions forms a silicon-silicon bond which will have a finite lifetime dependent on the decomposition paths which are available to it. In the case of alkyl radicals only the combination of thermalized methyl radicals shows any third body dependence at the pressures used in this study ($p > 10$ torr). The decomposition path of lowest energy for ethane is dissociation to two methyl radicals however, so that only the thermal energy of the combining methyl radicals has to be dissipated for stabilization. The same does not apply for silyl radicals. Pyrolysis studies of silanes indicate that decomposition paths with energy requirements significantly less than those necessary for homolysis of the silicon-silicon bond are available (45-47).

Consider the combination of two monosilyl radicals. If we accept the electron impact value for $\Delta H_f°(SiH_3) = 50$ kcal/mole (20) the disilane formed in reaction [48],



$$SiH_3 + SiH_3 \longrightarrow Si_2H_6^{\ddagger} \qquad [48]$$

will contain 83 kcal/mole excess energy when the radicals are thermalized since,

$$\Delta H_{48} = \Delta H_f°(Si_2H_6) - 2\Delta H_f°(SiH_3)$$

$$= 17.1 - 2 \times 50$$

$$= -83 \text{ kcal/mole.}$$

Pyrolysis of disilane has shown that the molecule decomposes to $SiH_2 + SiH_4$ with a rate constant of $k = 5.8 \times 10^{14} e^{-48900/RT}$ sec^{-1} (46,47). This represents a low energy path for the decomposition of the chemically activated disilane molecule. To a first approximation the unimolecular rate constant for decomposition of a molecule which contains significantly greater amounts of energy than is required for decomposition along the lowest energy path is given by the RRK expression

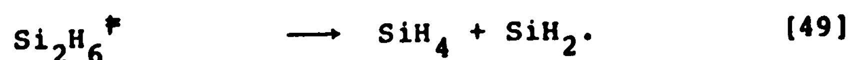
$$k_{uni} = A\left(\frac{E_{total} - E_a}{E_{total}}\right)^{s-1} \quad sec^{-1}$$

where $s = (3N-6)/2$, the number of effective oscillators at room temperature and A is the A factor of the Arrhenius

expression. Substituting the values given above for disilane the rate constant is found to be

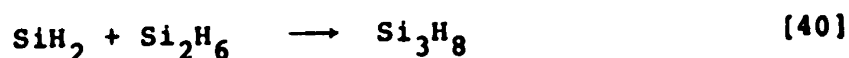
$$k_{uni} = 5.8 \times 10^{14} \left(\frac{83 - 49}{83}\right)^{8} = 4.6 \times 10^{11}\ \mathrm{sec}^{-1}$$

which requires a half-quenching pressure of some 250 atmospheres. The combination of monosilyl radicals then is an efficient path for disproportionation of monosilyl radicals to a silane molecule plus silylene.



$$Si_2H_6^{\ddagger} \longrightarrow SiH_4 + SiH_2. \qquad [49]$$

The silylene which will be in the singlet ground state may undergo further reactions by either inserting into a silicon hydrogen bond of disilane



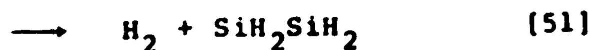
$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \qquad [40]$$

or terminating at the wall as a unit of polymer,

$$SiH_2 \xrightarrow{\text{wall}} \text{polymer}. \qquad [42]$$

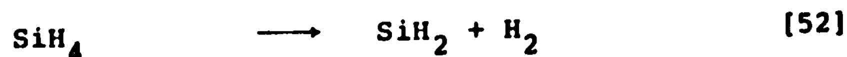
Reaction [49] is not the only low-energy decomposition path open to the excited disilane molecule, it may also lose a molecule of hydrogen which can happen either of two ways, 1,1 elimination as in [50] or 1,2 elimination as in [51].

$$Si_2H_6^{\ddagger} \longrightarrow H_2 + SiHSiH_3 \qquad [50]$$



$$\longrightarrow H_2 + SiH_2SiH_2 \qquad [51]$$

There are no kinetic data on these reactions but the enthalpy changes associated with them can be estimated using monosilane as a model compound. The activation energy for the thermolysis of monosilane to $H_2 + SiH_2$ is reported to be 56 kcal/mole (36). When this is combined with the activation energy for the thermal decomposition of disilane the heat of formation of SiH_2 can be calculated. Consider the two reactions,



$$SiH_4 \longrightarrow SiH_2 + H_2 \qquad [52]$$

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \qquad [49]$$

The enthalpy change for reaction [52] is given by

$$\Delta H_{52}^\circ = \Delta H_f^\circ(SiH_2) + \Delta H_f^\circ(H_2) - \Delta H_f^\circ(SiH_4)$$

where

$$E_{52} - E_{-52} = \Delta H_f^\circ(SiH_2) + \Delta H_f^\circ(H_2) - \Delta H_f^\circ(SiH_4),$$

and the heat of formation of SiH_2 is,

$$\Delta H_f^\circ(SiH_2) = 7.3 - 0 + 56 - E_{a_{-52}}$$

$$= 63 - E_{-52} \text{ kcal/mole.}$$

Similarly, for reaction [49]

$$\Delta H_{49}^\circ = \Delta H_f^\circ(SiH_2) + \Delta H_f^\circ(SiH_4) - \Delta H_f^\circ(Si_2H_6)$$

$$E_{49} - E_{-49}^\circ = \Delta H_f^\circ(SiH_2) + 7.3 - 17.1$$

and

$$\Delta H_f°(SiH_2) = 49 + 17.1 - 7.3$$

$$= 58.8 - E_{-49} \text{ kcal/mole.}$$

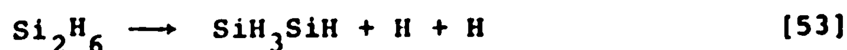
The heat of formation of SiH_2 therefore is less than 59 kcal/mole by an amount corresponding to the activation energy for the insertion of SiH_2 into a silicon hydrogen bond of monosilane. The insertion must have a positive activation energy associated with it since silylene preferentially inserts into methylsubstituted silanes in the presence of disilane (48) but the magnitude cannot be more than a few kilocalories since the insertion is observed at room temperature (60,61). A value of 6 kcal/mole was chosen for $E_{a_{-49}}$ which gives the value $\Delta H_f°(SiH_2) = 53$ kcal/mole, for the standard heat of formation of silylene. Thus the energy required to remove two hydrogen atoms from monosilane is 150 kcal/mole. Returning now to the case of disilane and reactions [50] and [51] a reasonable estimate for the removal of two hydrogen atoms from one end of disilane is also 150 kcal/mole since the dissociation energy of the first hydrogen bond is 5 kcal less than it is in monosilane (23) but the silyl group has a destabilizing effect on the radical. The value for the heat of formation of SiH_3SiH derived in this manner is given by,

$$\Delta H_{53}° = 2 \times \Delta H_f°(H) + \Delta H_f°(SiH_3SiH) - \Delta H_f°(Si_2H_6)$$

$$\Delta H_f°(SiH_3SiH) = 150 - 2 \times 52.1 + 17.1$$

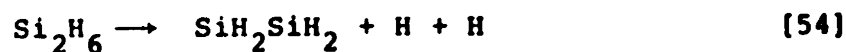
$$= 63 \text{ kcal/mole,}$$

from the reaction



$$Si_2H_6 \longrightarrow SiH_3SiH + H + H \qquad [53]$$

If the hydrogen atoms are removed one from either end of the disilane molecule the energy requirement will be greater since the two unpaired electrons do not form a stable π bond. The energy input to break the two bonds will not be much different from 180 kcal/mole. The enthalpy change for [54]



$$Si_2H_6 \longrightarrow SiH_2SiH_2 + H + H \qquad [54]$$

then becomes

$$\Delta H_{54}° = 2 \times \Delta H_f°(H) + \Delta H_f°(SiH_2SiH_2) - \Delta H_f°(Si_2H_6)$$

and the heat of formation,

$$\Delta H_f°(SiH_2SiH_2) = -2 \times 52.1 + 17.1 + 180$$

$$= 93 \text{ kcal/mole.}$$

It is now possible to estimate the enthalpy changes in reactions [50] and [51];

$$\Delta H_{50}° = \Delta H_f°(H_2) + \Delta H_f°(SiHSiH_3) - \Delta H_f°(Si_2H_6)$$

$$= 0 + 63 - 17.1$$

$$= 46 \text{ kcal/mole}$$

and

$$\Delta H_{51}° = \Delta H_f°(H_2) + \Delta H_f°(SiH_2SiH_2) - \Delta H_f°(Si_2H_6)$$
$$= 76 \text{ kcal/mole.}$$

Step [51] obviously will not contribute significantly to the decomposition of the chemically activated disilane molecule but reaction path [50] is energetically feasible. The absence of hydrogen among the products when methyl radicals reacted with disilane even though monosilane was present, suggests that the reverse of reaction [50] must have a significant energy of activation, as would indeed be expected for the insertion of SiH_3SiH into a hydrogen molecule. The activation energy for insertion of SiH_2 into H_2 is 4 kcal/mole greater than for the insertion into SiH_4 and the latter activation energy was assigned the value 6 kcal/mole. A value of 13 - 14 kcal/mole would then not be unreasonable for the insertion of SiH_3SiH into H_2 which means that E_{50} = 60 kcal/mole compared to a value of 49 kcal/mole for step [49]. Thus reaction [49] will be the predominant mode of decomposition of the chemically activated disilane.

Monosilyl radicals may also combine with disilanyl radicals to form a trisilane molecule containing excess energy

$$SiH_3 + Si_2H_5 \longrightarrow Si_3H_8^{\ddagger} \qquad [55]$$

In order to compute the exothermicity of this reaction a knowledge of the heat of formation of the disilanyl radical is mandatory. This can be obtained from the value for $D(Si_2H_5\text{-}H)$ of 90 kcal/mole estimated by Strausz et al. (23) and the values for the heats of formation of disilane and hydrogen atom.

For the decomposition

$$Si_2H_6 \longrightarrow Si_2H_5 + H \qquad [56]$$

the endothermicity is given by

$$\Delta H_{56}^\circ = \Delta H_f^\circ(H) + \Delta H_f^\circ(Si_2H_5) - \Delta H_f^\circ(Si_2H_6),$$

whence

$$\Delta H_f^\circ(Si_2H_5) = 90 + 17.1 - 52.1$$
$$= 55 \text{ kcal/mole.}$$

Substituting this value into the expression for the enthalpy change in [55] (130,131),

$$\Delta H_{55}^\circ = \Delta H_f^\circ(Si_3H_8) - \Delta H_f^\circ(Si_2H_5) - \Delta H_f^\circ(SiH_3)$$
$$= 25.9 - 55 - 50$$
$$= -79 \text{ kcal/mole}$$

we get a contribution of 79 kcal/mole to the energy of the molecule by the newly-formed bond. This is 5 kcal/mole less than the value found for the silicon-silicon bond in disilane which suggests that 55 kcal/mole is a minimum value for the heat of formation of the disilanyl

radical. No value has been reported for the energy of activation for the thermal decomposition of trisilane which is postulated to proceed via elimination of a silylene (45-47). If the Arrhenius A-factor for the decomposition of trisilane is similar to that for disilane and monosilane the rate constant at 592°K corresponds to an E_a of 48 kcal/mole (46). When these values are substituted into the RRK expression,

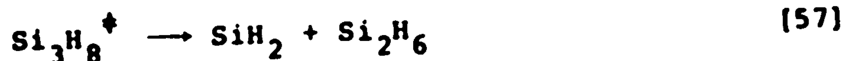
$$k_{decomp} = 5.8 \times 10^{14} \left(\frac{79 - 48}{79}\right)^{12.5} \sec^{-1}$$

$$= 4.7 \times 10^{9} \sec^{-1}$$

the rate constant for decomposition is such that approximately one atmosphere of substrate pressure is required to quench half of the excited molecules if each collision is effective. The recombination of a silyl and disilanyl radical is not a probable source of product trisilane at the pressures used in this work.

The number of potential decomposition paths for the chemically activated trisilane is considerably greater than it was for disilane. Only those paths which entail Si-Si bond scission will be considered because of the observed absence of hydrogen in systems where hydrogen atoms were not present.

Specifically, reactions [57] and [58],



$$Si_3H_8^{\ddagger} \longrightarrow SiH_2 + Si_2H_6 \qquad [57]$$

$$\longrightarrow SiHSiH_3 + SiH_4 \qquad [58]$$

which correspond to the two types of disproportionations between mono- and disilanyl radicals, will be treated. The enthalpy changes for [57],

$$H_{57}^\circ = \Delta H_f^\circ(SiH_2) + \Delta H_f^\circ(Si_2H_6) - \Delta H_f^\circ(Si_3H_8)$$

$$= 53 + 17.1 - 25.9$$

$$= 44 \text{ kcal/mole.}$$

and for [58]

$$H_{58}^\circ = \Delta H_f^\circ(SiHSiH_3) + \Delta H_f^\circ(SiH_4) - \Delta H_f^\circ(Si_3H_8)$$

$$= 63 + 7.3 - 25.9$$

$$= 44 \text{ kcal/mole}$$

are the same, which means that the activation energy for [-58] must be greater than that for the back reaction [-57] in order for elimination of SiH_2 to be observed in the pyrolysis of trisilane. The magnitude of the difference $E_{-58} - E_{-57}$ determines how much monosilane is produced in the reaction sequence [55] + [58] and together with the monosilane, the substituted silylene SiH_3SiH whose main mode of removal will be polymerization,

$$SiHSiH_3 \xrightarrow{\text{wall}} \text{polymer} \qquad [41]$$

Thermodynamic properties of tetrasilane, the product of the combination of two disilanyl radicals, have not been reported. The heat of formation is estimated to

be 35 kcal/mole from the average thermochemical bond energies of trisilane and the heats of formation of the atoms. The similarity between the energies of activation for the thermolyses of di- and tri-silane suggest that the activation energy of decomposition of tetrasilane will be closely approximated by 45 kcal/mole.

The chemically activated tetrasilane formed in reaction [59]

$$Si_2H_5 + Si_2H_5 \longrightarrow Si_4H_{10}^{*} \qquad [59]$$

possesses energy above its ground state energy, given by the enthalpy change,

$$\Delta H_{59}^{\circ} = \Delta H_f^{\circ}(Si_4H_{10}) - 2\Delta H_f^{\circ}(Si_2H_5)$$

$$= 35 - 2 \times 55$$

$$= -75 \text{ kcal/mole.}$$

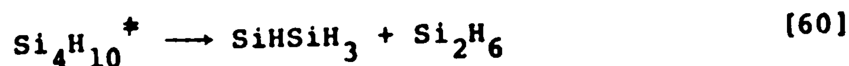
The greater number of effective oscillators in the RRK expression lowers k_{uni}

$$k_{uni} = 5.8 \times 10^{14} \left(\frac{75 - 45}{75}\right)^{17}$$

$$= 9.2 \times 10^{7} \text{ sec}^{-1}$$

to a value such that 20 torr of substrate is sufficient to stabilize half of the excited molecules if every collision is effective.

The products of the breakdown of the excited tetrasilane molecule do not include significant amounts of trisilane since it was observed in the pressure study of the mercury sensitization of disilane that the trisilane yield did not increase at low pressures where all of the tetrasilane was not stabilized. This observation points up the approximate nature of the values which were used to get the various heats of formation since thermodynamically the more favorable path for decomposition of the tetrasilane is a breakdown to $SiH_2 + Si_3H_8$; see the following reactions,



$$Si_4H_{10}^{*} \longrightarrow SiHSiH_3 + Si_2H_6 \qquad [60]$$

$$\longrightarrow SiH_2 + Si_3H_8 \qquad [61]$$

The enthalpy changes for the two reactions are given by

$$\Delta H_{60}° = \Delta H_f°(SiHSiH_3) + \Delta H_f°(Si_2H_6) - \Delta H_f°(Si_4H_{10})$$

$$= 63 + 17.1 - 35$$

$$= 45 \text{ kcal/mole},$$

and

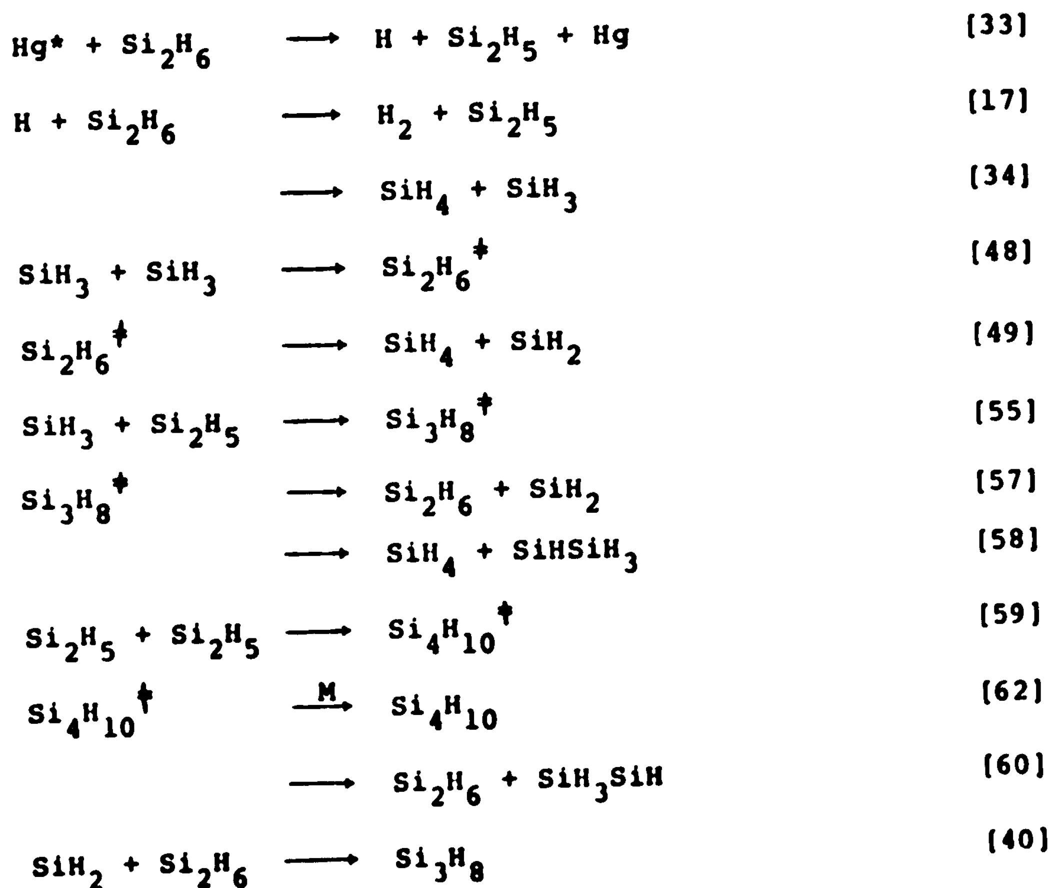
$$\Delta H_{61}° = \Delta H_f°(SiH_2) + \Delta H_f°(Si_3H_8) - \Delta H_f°(Si_4H_{10})$$

$$= 44 \text{ kcal/mole}.$$

The difference in $\Delta H°$'s is compatible with the observed products if the activation energies of the reverse reactions are different, but in order for [60]

to predominate over [61] there must exist a higher energy barrier for the insertion of SiH_2 into a primary silicon hydrogen bond of trisilane than for the insertion of silylsilylene, SiH_3SiH, into a silicon hydrogen bond of disilane.

More and better thermochemical data will no doubt resolve this enigma. In the meantime, the above treatment is consistent with the observed data and suggests the following mechanism for the mercury sensitization of disilane at room temperature.



$$Hg^* + Si_2H_6 \longrightarrow H + Si_2H_5 + Hg \qquad [33]$$

$$H + Si_2H_6 \longrightarrow H_2 + Si_2H_5 \qquad [17]$$

$$\longrightarrow SiH_4 + SiH_3 \qquad [34]$$

$$SiH_3 + SiH_3 \longrightarrow Si_2H_6^{\ddagger} \qquad [48]$$

$$Si_2H_6^{\ddagger} \longrightarrow SiH_4 + SiH_2 \qquad [49]$$

$$SiH_3 + Si_2H_5 \longrightarrow Si_3H_8^{\ddagger} \qquad [55]$$

$$Si_3H_8^{\ddagger} \longrightarrow Si_2H_6 + SiH_2 \qquad [57]$$

$$\longrightarrow SiH_4 + SiHSiH_3 \qquad [58]$$

$$Si_2H_5 + Si_2H_5 \longrightarrow Si_4H_{10}^{\ddagger} \qquad [59]$$

$$Si_4H_{10}^{\ddagger} \xrightarrow{M} Si_4H_{10} \qquad [62]$$

$$\longrightarrow Si_2H_6 + SiH_3SiH \qquad [60]$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \qquad [40]$$

$$SiH_2 \xrightarrow{wall} \text{polymer} \qquad [42]$$

$$Si_2H_4 \xrightarrow{wall} \text{polymer} \qquad [41]$$

A steady-state treatment of these reactions, taking

$$2k_{48} = k_{55} = 2k_{59}$$

to simplify the quadratic expressions for the radical concentrations, gives the following relations for the quantum yields of the products taken at time zero.

$$\Phi_{H_2} = \frac{k_{17}}{k_{17}+k_{34}} = 0.58 \qquad [63]$$

$$\Phi_{SiH_4} = \frac{k_{33}}{k_{17}+k_{34}} + \tfrac{1}{4}\left(1 - \frac{k_{17}}{k_{17}+k_{34}}\right)^2 + \left(\frac{k_{58}}{k_{57}+k_{58}}\right)(\tfrac{1}{4}) \left\{1 - \left(\frac{k_{17}}{k_{17}+k_{34}}\right)^2\right\} = 0.73 \qquad [64]$$

$$\Phi_{Si_3H_8} = \frac{k_{40}[Si_2H_6]}{k_{40}[Si_2H_6]+k_{42}} \left\{ \tfrac{1}{4}\left(1 - \frac{k_{17}}{k_{17}+k_{34}}\right)^2 + \left(\frac{k_{57}}{k_{57}+k_{58}}\right)(\tfrac{1}{4}) \left\{1 - \left(\frac{k_{17}}{k_{17}+k_{34}}\right)^2\right\}\right\} = 0.10 \qquad [65]$$

$$\Phi_{Si_4H_{10}} = \frac{k_{62}[M]}{k_{62}[M]+k_{60}} \left\{(\tfrac{1}{4})\left(1 + \frac{k_{17}}{k_{17}+k_{34}}\right)^2\right\} = 0.67 \qquad [66]$$

From these, various rate constant ratios are derived by the appropriate substitutions. Substituting [63] into [64]

$0.73 = 0.42 + \frac{1}{4}(1 - 0.58)^2 + k_{58}/(k_{57}+k_{58})(\frac{1}{2})\{1 - (0.58)^2\}$

we get

$$\frac{k_{58}}{k_{57}+k_{58}} = 0.80 \qquad [67]$$

Further substitution of [63] and [67] into [65] gives,

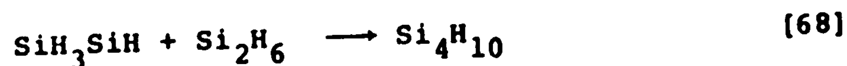
$$\frac{k_{40}[Si_2H_6]}{k_{40}[Si_2H_6] + k_{42}} = 0.91$$

and substitution of [63] into [66] gives,

$$\frac{k_{62}[M]}{k_{62}[M] + k_{60}} = 1.$$

The large value for the ratio $k_{58}/(k_{57}+k_{58})$ suggests that further, more quantitative work on the pyrolysis of trisilane will show that the elimination of monosilane is the major primary step in the decomposition rather than elimination of SiH_2 as is presently postulated. The fact that $k_{40}[Si_2H_6]/(k_{40}[Si_2H_6] + k_{42})$ is close to unity shows the facility of the insertion of silylene into the silicon hydrogen bond of disilane even at room temperature as compared to diffusion to the wall. A comment on the ratio for stabilization of tetrasilane versus unimolecular decomposition is in order. The observation that this ratio is unity implies that all disilanyl radicals which

become a stable tetrasilane molecule under the conditions employed in the time study. It also suggests that the assumption that step [41] is the sole fate of the SiH_3SiH radical formed from the disproportionation of silyl and disilyl radicals, is not valid, rather, some of these diradicals insert into the substrate to give tetrasilane via [68]



$$SiH_3SiH + Si_2H_6 \longrightarrow Si_4H_{10} \qquad [68]$$

The treatment so far has ignored the dependence of the tetrasilane yield on the disilane pressure which is observed in Figures III-1 and III-2. Since the expression for the quantum yield of tetrasilane is given by

$$\Phi_{Si_4H_{10}} = \frac{k_{62}[M]}{k_{62}[M]+k_{60}} \left\{ \tfrac{1}{4} \left(1 + \frac{k_{17}}{k_{17}+k_{34}}\right)^2 \right\},$$

the reciprocal,

$$\frac{1}{\Phi_{Si_4H_{10}}} = b + \left\{ 1 + \frac{k_{60}}{k_{55}[M]} \right\},$$

where

$$b = 4\left(1 + \frac{k_{17}}{k_{17}+k_{34}}\right)^{-2},$$

gives a straight line graph. The intercept can be compared with the value derived from the extrapolation to zero time.

The results from Si_2D_6 and Si_2H_6 are plotted in Figures III-13 and III-14 and the slope in both cases is the same and equal to

$$\left(\frac{k_{60}}{k_{62}}\right) \times b = 100 \text{ torr.}$$

For the Si_2D_6 case where the intercept b = 1.67 as compared to the calculated 1.60, the ratio

$$\frac{k_{60}}{k_{62}} = \frac{100 \text{ torr}}{1.67} \times 5.38 \times 10^{-8} \frac{\text{moles/cc}}{\text{torr}} = 3.22 \times 10^{-6} \text{ moles/cc.}$$

This corresponds to a half-quenching pressure of 60 torr of disilane. The RRK calculation for tetrasilane gave a rate constant of 9.2×10^7 sec^{-1} for its unimolecular decomposition, and by adopting a value of 4.5Å for the collision diameter of Si_2D_6, the collision number in the simple collision theory, is 4.5×10^{14} cc/mole-sec. The efficiency of Si_2D_6 as a quencher of $Si_4D_{10}^{\ddagger}$ is then given by the relation

$$\frac{(k_{60})_{RRK}}{(k_{60}/k_{62})} \div Z = \frac{1}{16}$$

i.e., one collision in sixteen is effective in stabilizing the excited molecules. Alternatively, since the molecules contain 30 kcal/mole excess energy, where the energy is removed with equal probability per collision, 1.9 kcal is

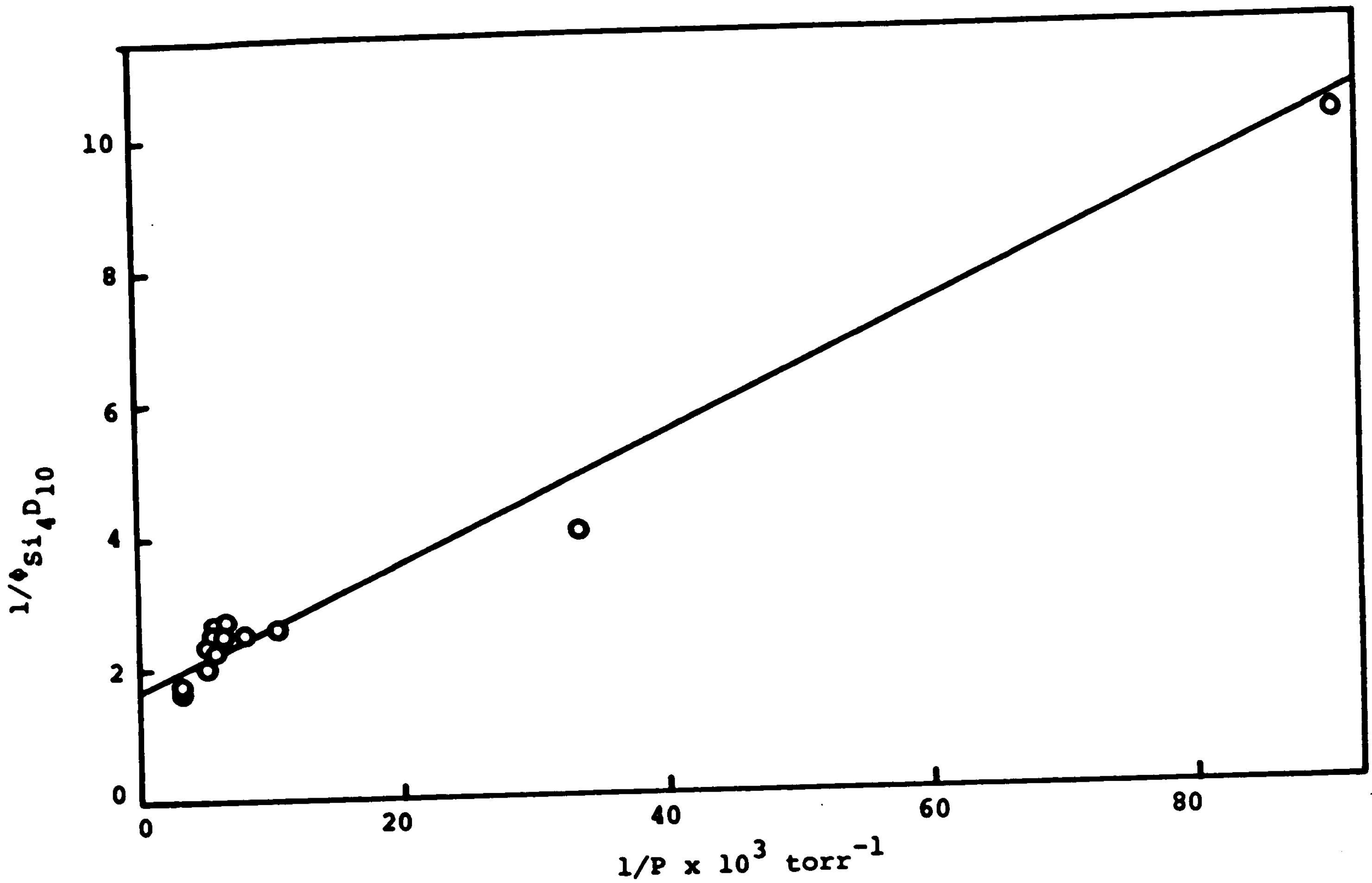


FIGURE III-13: Reciprocal of Si_4D_{10} quantum yield versus reciprocal of substrate pressure.

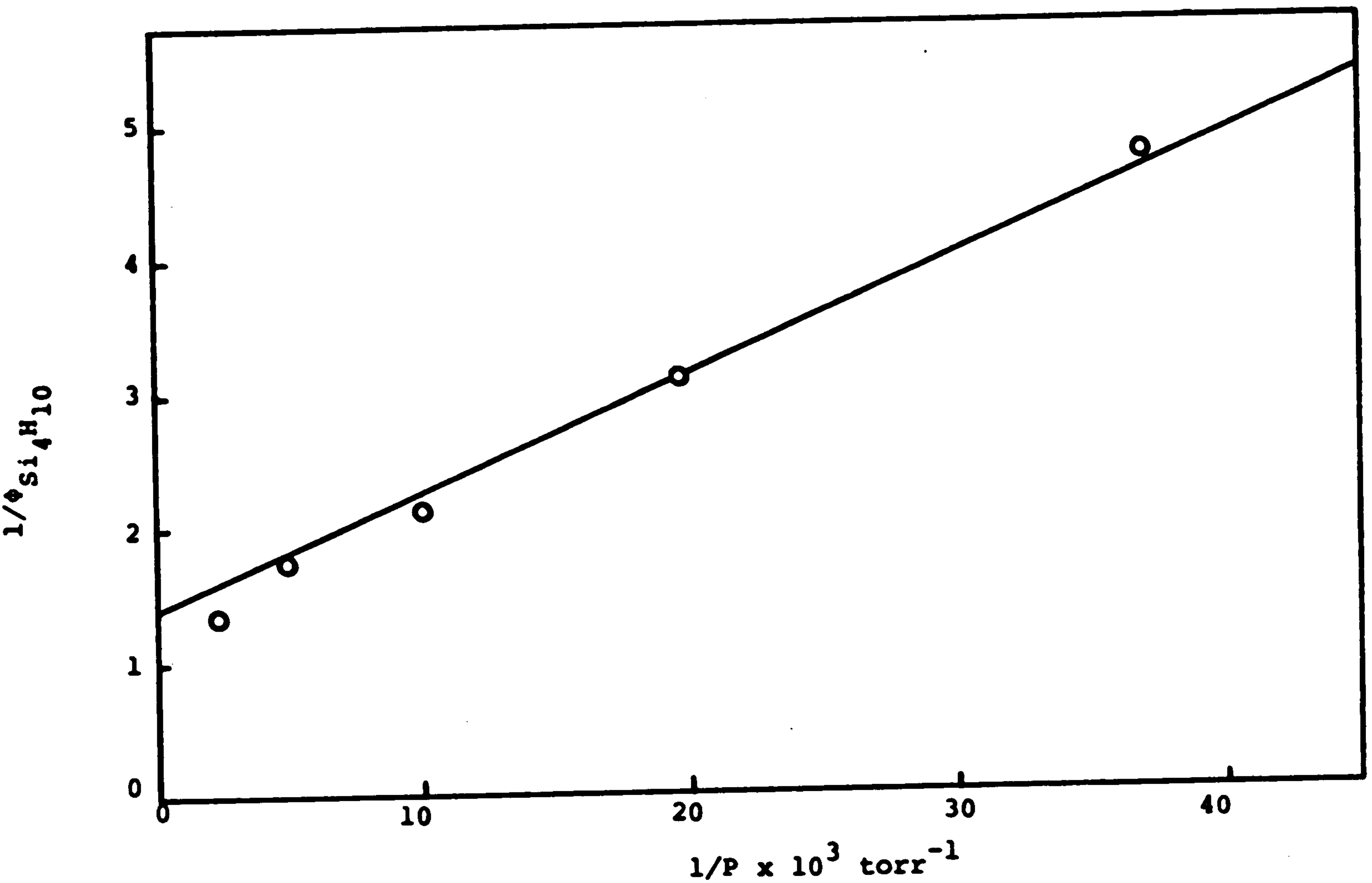
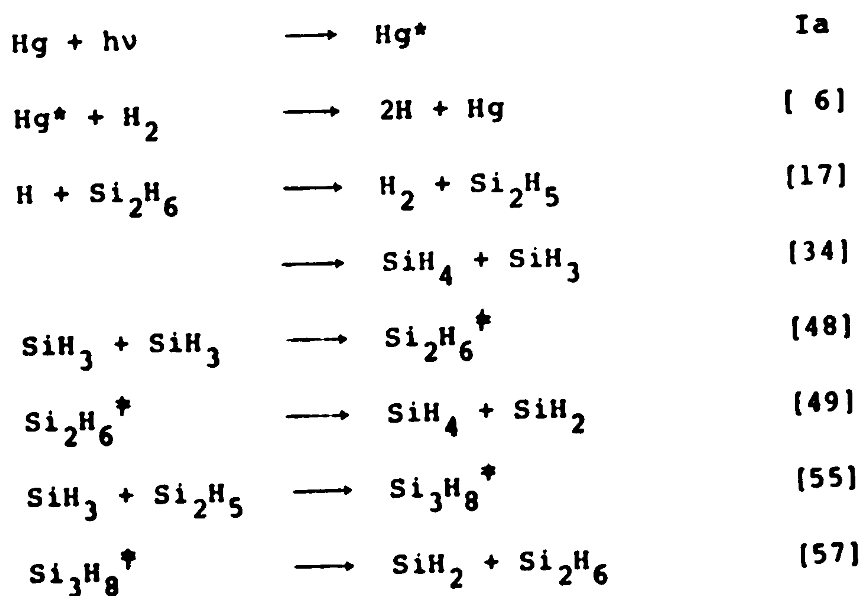


FIGURE III-14: Reciprocal of Si_4H_{10} quantum yield vs reciprocal of substrate pressure.

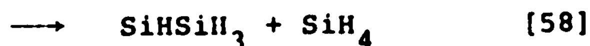
removed per collision. The raw data do not lend themselves to a more sophisticated treatment wherein more definite limits can be set on the amounts of energy transferred and the frequency with which it is transferred. Future studies on the recombination of silyl radicals, when more and better thermodynamic values are known, certainly will contribute to the understanding of the processes of energy randomization and energy transfer.

b) Hydrogen atoms plus disilane

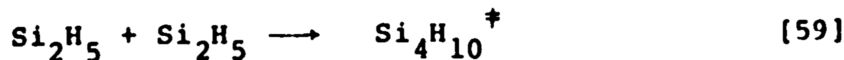
Hydrogen atoms produced from the mercury photosensitization of hydrogen were found to react with disilane to produce both monosilyl and disilanyl radicals which in turn may undergo disproportionation and combination as in the case of the mercury photosensitization of disilane, viz.,



$Hg + h\nu$	$\longrightarrow$	Hg^{*}	Ia
$Hg^{*} + H_2$	$\longrightarrow$	$2H + Hg$	[6]
$H + Si_2H_6$	$\longrightarrow$	$H_2 + Si_2H_5$	[17]
	$\longrightarrow$	$SiH_4 + SiH_3$	[34]
$SiH_3 + SiH_3$	$\longrightarrow$	$Si_2H_6^{\dagger}$	[48]
$Si_2H_6^{\dagger}$	$\longrightarrow$	$SiH_4 + SiH_2$	[49]
$SiH_3 + Si_2H_5$	$\longrightarrow$	$Si_3H_8^{\dagger}$	[55]
$Si_3H_8^{\dagger}$	$\longrightarrow$	$SiH_2 + Si_2H_6$	[57]

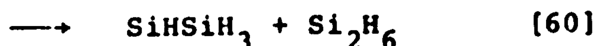


$$\longrightarrow \quad SiHSiH_3 + SiH_4 \qquad [58]$$

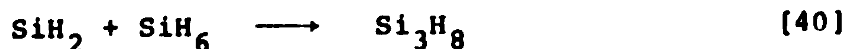


$$Si_2H_5 + Si_2H_5 \longrightarrow Si_4H_{10}^{\ddagger} \qquad [59]$$

$$Si_4H_{10}^{\ddagger} \xrightarrow{M} Si_4H_{10} \qquad [62]$$



$$\longrightarrow \quad SiHSiH_3 + Si_2H_6 \qquad [60]$$



$$SiH_2 + SiH_6 \longrightarrow Si_3H_8 \qquad [40]$$

$$SiH_2 \xrightarrow{wall} \text{polymer} \qquad [42]$$

$$Si_2H_4 \xrightarrow{wall} \text{polymer} \qquad [41]$$

The simplifying assumptions, that $2K = 2k_{48} = k_{55} = 2k_{59}$ and that vibrationally excited disilane and trisilane molecules cannot be stabilized, are made and the steady-state approximations then give the following expressions for the quantum yields of products,

$$\Phi_{monosilane} = \frac{2k_{34}}{k_{17}+k_{34}} + \left(\frac{k_{34}}{k_{17}+k_{34}}\right)^2 + \frac{k_{58}}{k_{57}+k_{58}} \left(\frac{k_{17}k_{34}}{(k_{17}+k_{34})^2}\right) \qquad [69]$$

$$\Phi_{trisilane} = \frac{k_{40}[Si_2H_6]}{k_{40}[Si_2H_6]+k_{42}} \left\{\left(\frac{k_{34}}{k_{17}+k_{34}}\right)^2 + \frac{k_{57}}{k_{57}+k_{58}} \left(\frac{k_{17}k_{34}}{(k_{17}+k_{34})^2}\right)\right\} \qquad [70]$$

$$\Phi_{tetrasilane} = \frac{k_{62}[M]}{k_{62}[M]+k_{60}} \left\{ \frac{k_{17}}{k_{17}+k_{34}} \right\}^2 \qquad [71]$$

Substituting the values derived from equations [63] - [67] from section a) into [69], [70] and [71] the predicted quantum yields are,

Φ monosilane = 0.84 + 0.176 + 0.195 = 1.21

Φ trisilane = 0.91 (0.176 + 0.049) = 0.22

Φ tetrasilane = 1 (0.34) = 0.34.

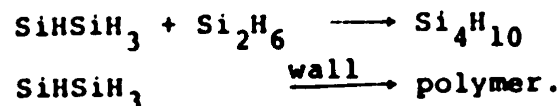
This distribution of products is similar to that observed in Table III-IX where the measured values are,

Φ monosilane = 0.9

Φ trisilane = 0.2

and Φ tetrasilane = 0.2.

These results indicate that all of the disilanyl radicals which combine are being recovered as tetrasilane molecules since a quantum yield of 0.2 for Si_4D_{10} is not abnormal. This in turn means that the main function that C_3D_8 served in the H_2 + Si_2H_6 + Hg* system was to act as a competitor with hydrogen for the excited mercury atoms. There is then no reason to postulate that the observed dependence of the Si_4D_{10} yield on the disilane-d_6 pressure is due to a competition between an intermediate reacting with disilane to produce tetrasilane and the same intermediate being removed in a unimolecular reaction, such as



$$SiHSiH_3 + Si_2H_6 \longrightarrow Si_4H_{10}$$
$$SiHSiH_3 \xrightarrow{wall} \text{polymer.}$$

Further consideration will now be given to the initial interaction between the hydrogen atoms and the disilane molecule. The rate constants for the reaction between hydrogen atoms and simple silanes and methylsubstituted silanes are known to be large (55,56,132,133). Some pertinent rate constant ratios derived from relative rate studies are presented in Table XX together with some estimated Arrhenius rate equation parameters reported by the authors. There is excellent agreement among the observed ratios considering that the results were obtained by three different methods; a fast flow system (132), direct photolysis of ethylene (133), and the present mercury photosensitization. The agreement between the quoted rate constants is not as striking, this reflects the current controversy over the absolute rate constants for the addition of hydrogen atoms to olefins. For example, two recent values for the rate constant for H + C_2H_4, both determined by Lyman-α photometry, are 2.3×10^{11} cc/mole-sec (134-136) and 8.1×10^{11} cc/mole-sec (138). The lower value is used in the computations which follow.

The Arrhenius A factors in the expression $k = Ae^{-Ea/RT}$, for the metathetical reactions between methyl and trifluoromethyl radicals and silanes were found to be the same as those for metatheses with the corresponding alkanes (23,73-86). It is assumed that

the same is true for the abstraction of hydrogen from disilane by hydrogen atoms. The Arrhenius parameters for the alkane case, $H + C_2H_6$, are

$$\log k \text{ abstraction} = 14.1 - 9.7/\theta \ (139),$$

when k is expressed in cc/mole-sec and $\theta = 2.303$ RT. The ratio of abstraction to total reaction between H atoms and disilane is given in equation [63] as,

$$\frac{k_{17}}{k_{17}+k_{34}} = 0.58 \qquad [63]$$

and the ratio of the rate constants for the total reaction of hydrogen atoms with disilane to the rate constant for the reaction of hydrogen atoms with ethylene is 3.2 (see Table III-XV). The absolute value of k_{17} then becomes,

$$k_{17} = 0.58 \times 3.2 \times 2.3 \times 10^{11} = 4.3 \times 10^{11} \text{ cc/mole-sec.}$$

When k_{17} is expressed in its Arrhenius form, $k_{17} = A_{17}$ $e^{-E/RT}$, and the values for k_{17} and A_{17} are inserted, the energy of activation

$$E_{17} = (14.1 - 11.63)\ 1.38 = 3.4 \text{ kcal/mole.}$$

Arrhenius parameters can also be calculated for the rate constant of the displacement reaction, [34]. Using the values derived from the slope in Figure 10,

$$E_{17} - E_{34} = 0.50 \pm 0.24 \text{ kcal/mole,}$$

TABLE III - XV

Rate Constant Ratios and Estimated Arrhenius Parameters for Reactions Between H Atoms and Various Silanes as Compared to the Addition Reaction for H Atoms plus Olefins

Reaction	Olefin	Observed Ratio	k Abstraction Relative H + C_2H_4	Log k total $\frac{cc}{mole-sec}$	Log k Abstraction $\frac{cc}{mole-sec}$	Log A $\frac{cc}{mole-sec}$	E_a $\frac{kcal}{mole}$	Ref.
H + SiH_4							8	56
H + SiH_4							0.5	55
H + SiH_4	cis-butene-2	0.27	0.19[a]		11.12[f,d]	14.1	4	132
H + Si_2H_6	ethylene	3.2	1.9[b]	11.86[c]	11.63	14.1	3	This work
H + Si_2D_6	ethylene	1.7		11.59[c]				This work
D + SiH_4	ethylene-d_4	0.53	0.53		11.50[e]			133
D + Si_2H_6	ethylene-d_4	5.0	5.0		12.47[e]			133

TABLE III - XV (cont'd)

(a) $\frac{k_{H\ +\ cis\text{-}butene\text{-}2}}{k_{H\ +\ C_2H_4}} = 0.72$; R. J. Cvetanovic and L. C. Doyle, J. Chem. Phys. 50, 4705 (1969).

(b) $\frac{k_{17}}{k_{17}+k_{34}} = 0.58$; equation [63].

(c) Based on $k_{H\ +\ C_2H_4} = 2.3 \times 10^{11}$ cc/mole-sec; Ref. 134-136.

(d) Based on $k_{H\ +\ cis\text{-}butene\text{-}2} = 4.9 \times 10^{11}$ cc/mole-sec; E. E. Daby and H. Niki, J. Chem. Phys. 51, 1255 (1969).

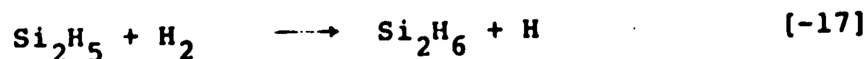
(e) Based on $k_{D\ +\ C_2D_4} = 6 \times 10^{11}$ cc/mole-sec; "best value" derived from literature values.

and

$$\log(A_{17}/A_{34}) = 0.61 \pm 0.15.$$

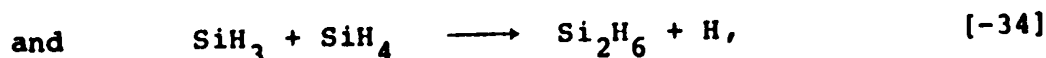
From these it follows that $\log k_{34} = 13.5 - 2.9/\theta$ when k_{34} is expressed in units of cc/mole-sec.

A measure of the kinetic importance of the reverse reactions,



$$Si_2H_5 + H_2 \longrightarrow Si_2H_6 + H \qquad [-17]$$

and



$$SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H, \qquad [-34]$$

which have been postulated in the pyrolysis studies, can be obtained from the following thermodynamic relations,

$$\log \frac{A \text{ forward}}{A \text{ reverse}} = \frac{\Delta S^\circ}{2.3\,R} \quad \text{and} \quad \Delta H^\circ = E_{a \text{ forward}} - E_{a \text{ reverse}},$$

and the appropriate thermodynamic properties listed in Table XXI.

The change in entropy for reaction [17] is expressed by $\Delta S_{17}{}^\circ = (S^\circ_{Si_2H_5} + S^\circ_{H_2}) - (S^\circ_{Si_2H_6} + S^\circ_H)$ cal/mole-deg. Substituting the values from Table III-XVI, this expression becomes

$$S^\circ_{17} = 5.7 \text{ cal/mole-deg},$$

and

$$\log \frac{A_{17}}{A_{-17}} = \frac{5.7}{2.3R} = 1.25,$$

whence $A_{-17} = 8 \times 10^{12}$ cc/mole-sec. The estimated value of E_{-17} is given by

TABLE III - XVI

Thermodynamic Properties

Species	S° cal/mole-deg	ΔH_f° kcal/mole
H_2	31.2[a]	0 [a]
SiH_4	48.7[a]	7.3[d]
Si_2H_6	6[illegible].1[a]	17.1[d]
H	27.4[a]	52.1[a]
SiH_3	50.2[b]	50 [e]
Si_2H_5	67 [c]	55 [f]

(a) Ref. 3, Table I - I.

(b) Estimated by assuming $S^\circ_{SiH_3} = S^\circ_{PH_3}$

(c) Estimated by assuming Si - H bond makes same contribution to S° in SiH_4 and Si_2H_6.

(d) Ref. 130.

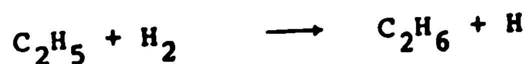
(e) Ref. 20.

(f) Estimated from $D(Si_2H_5 - H) = 90$ kcal/mole and assuming combination of H atoms and Si_2H_5 has no energy of activation.

$$E_{-17} = E_{17} - \Delta_f{}^\circ(Si_2H_5) - \Delta H_f{}^\circ(Si_2H_5) - \Delta H_f{}^\circ(H_2) + \Delta H_f{}^\circ(H)$$

$$= 17 \text{ kcal/mole.}$$

When the Arrhenius parameters for [-17], log $k_{-17} = 12.9 - 17/\theta$, are compared to the values for the carbon analogue,



$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H$$

which are reported to be, log $k_{C_2H_5} = 12.7 - 13.9/\theta$ (140), it is seen that not only are the pre-exponential A-factors similar but the activation energies differ only by some 3 kcal/mole.

Treating reaction [-34] in a similar manner it can be shown that, log $k_{-34} = 12.1 - 15/\theta$

from $S_{34}{}^\circ = (S_{SiH_4}{}^\circ + S_{SiH_3}{}^\circ) - (S_{Si_2H_6}{}^\circ + S_H{}^\circ)$

$$= 64 \text{ cal/mole-deg,}$$

and $E_{-34} = E_{34} - \Delta H_f{}^\circ(SiH_3) - \Delta H_f{}^\circ(SiH_4) + \Delta H_f{}^\circ(Si_2H_6) + \Delta H_f{}^\circ(H)$

$$= 15 \text{ kcal/mole,}$$

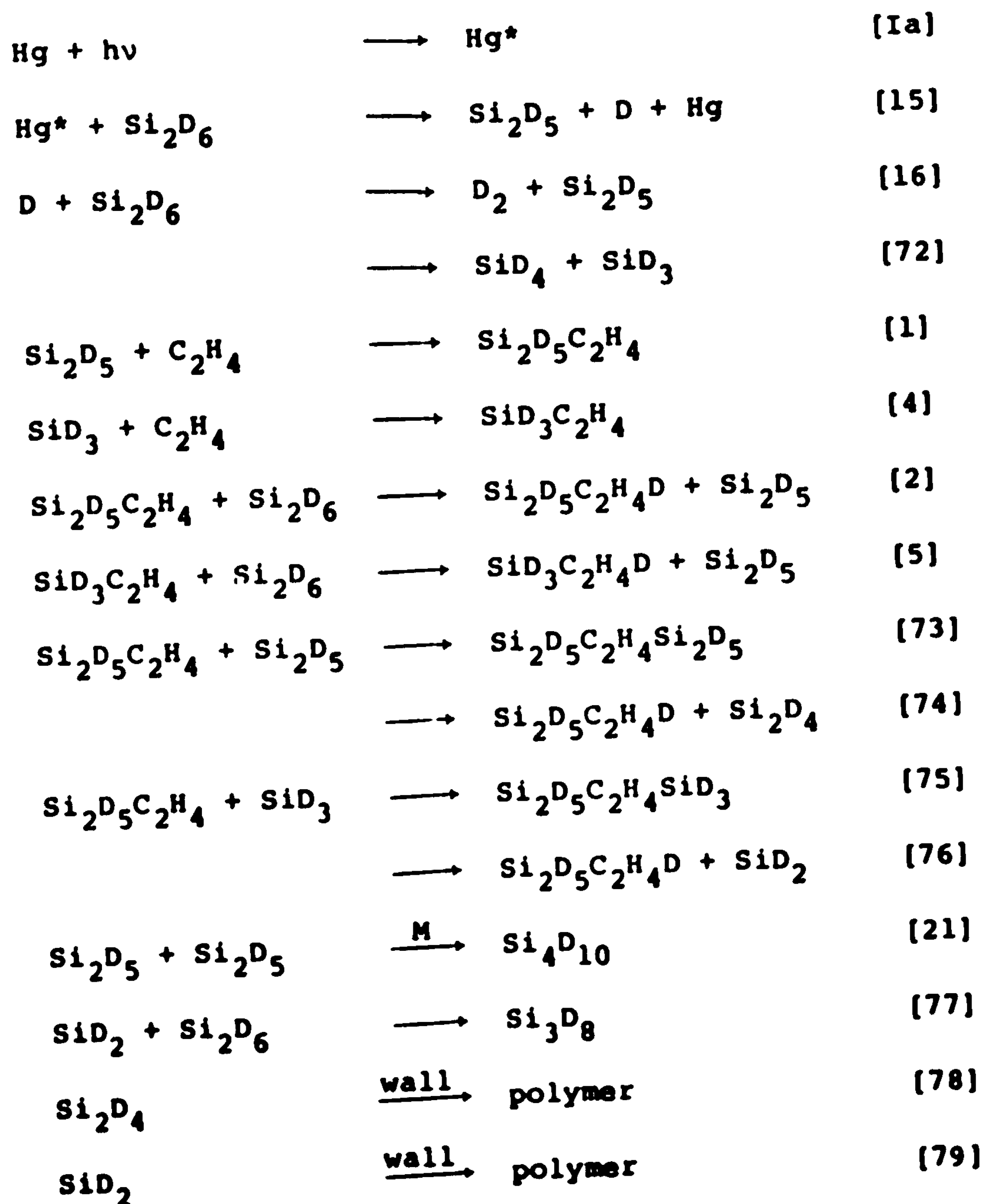
where $\log\left(\frac{A_{34}}{A_{-34}}\right) = \frac{\Delta S_{34}{}^\circ}{2.3R}$ and $E_{-34} = E_{34} - \Delta H_{34}{}^\circ$

The pre-exponential A-factor for reaction [-34], a displacement reaction, is similar to the A-factor for the abstraction reactions of alkyl radicals (86) and suggests that there is little steric hindrance associated with

step [-34].

c) Addition to ethylene

The mechanism proposed below accounts for the observed non-scavengable monosilane and trisilane and the monomers formed when silyl and disilanyl radicals add to the olefin ethylene.



$$Hg + h\nu \longrightarrow Hg^* \quad [Ia]$$

$$Hg^* + Si_2D_6 \longrightarrow Si_2D_5 + D + Hg \quad [15]$$

$$D + Si_2D_6 \longrightarrow D_2 + Si_2D_5 \quad [16]$$

$$\longrightarrow SiD_4 + SiD_3 \quad [72]$$

$$Si_2D_5 + C_2H_4 \longrightarrow Si_2D_5C_2H_4 \quad [1]$$

$$SiD_3 + C_2H_4 \longrightarrow SiD_3C_2H_4 \quad [4]$$

$$Si_2D_5C_2H_4 + Si_2D_6 \longrightarrow Si_2D_5C_2H_4D + Si_2D_5 \quad [2]$$

$$SiD_3C_2H_4 + Si_2D_6 \longrightarrow SiD_3C_2H_4D + Si_2D_5 \quad [5]$$

$$Si_2D_5C_2H_4 + Si_2D_5 \longrightarrow Si_2D_5C_2H_4Si_2D_5 \quad [73]$$

$$\longrightarrow Si_2D_5C_2H_4D + Si_2D_4 \quad [74]$$

$$Si_2D_5C_2H_4 + SiD_3 \longrightarrow Si_2D_5C_2H_4SiD_3 \quad [75]$$

$$\longrightarrow Si_2D_5C_2H_4D + SiD_2 \quad [76]$$

$$Si_2D_5 + Si_2D_5 \xrightarrow{M} Si_4D_{10} \quad [21]$$

$$SiD_2 + Si_2D_6 \longrightarrow Si_3D_8 \quad [77]$$

$$Si_2D_4 \xrightarrow{wall} \text{polymer} \quad [78]$$

$$SiD_2 \xrightarrow{wall} \text{polymer} \quad [79]$$

Ethyldisilane is generated in a chain reaction which is initiated by steps [15], [16] and [72], carried by [1], [2], [4] and [5], and terminated by [73] and [74]. The following expression is obtained for the steady-state concentration of Si_2D_5:

$$[Si_2D_5] = \left(\frac{I_a \quad k_2 \; [Si_2D_5]}{(k_{73}+k_{74}) k_1 [C_2H_4]} \right)^{\frac{1}{2}} \qquad [80]$$

The ratio of the quantum yield of tetrasilane in the absence of ethylene as derived in section 2a) to that in the presence of the olefin is,

$$\frac{\Phi° \text{tetrasilane}}{\Phi \text{ tetrasilane}} = 1 + \tfrac{1}{2} \left(1 + \frac{k_{16}}{k_{16}+k_{72}}\right)^2 \left(\frac{k_{73}+k_{74}}{k_{21}}\right)\left(\frac{k_1}{k_2}\right) \frac{[C_2H_4]}{[Si_2D_6]}$$

[81]

$\left(\frac{\Phi°_{Si_4D_{10}}}{\Phi_{Si_4D_{10}}} - 1\right)$ is plotted vs $[C_2H_4]$ in Figure III-15. The slope of the line, combined with the value of 0.58 for $\frac{k_{16}}{k_{16}+k_{72}}$ and the assumption that $2k_{21} = (k_{73}+k_{74})$, gives a value for k_1/k_2;

$$\frac{k_1}{k_2} = 4.6 \times 10^2.$$

The absolute value of k_2 is estimated from the determinations of the rate constants for the metathetical reaction between a series of simple alkyl radicals and disilane

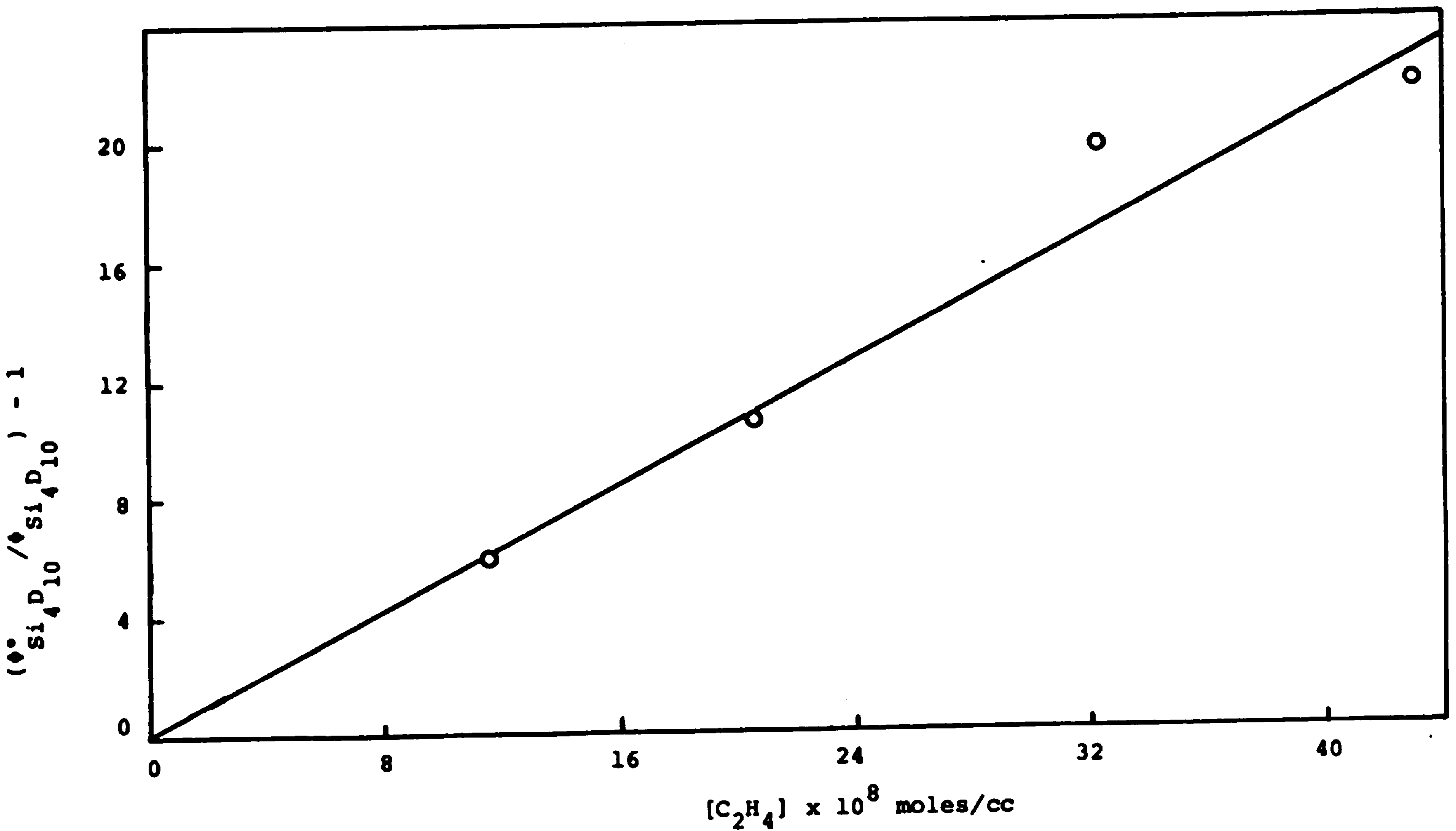


FIGURE III-15: A plot of the results from Table III-VI according to equation [81].

given in Table III-XVII, to be 1 x 10^7 cc/mole-sec. The rate constant for the addition of disilanyl to ethylene, k_1, is then 5 x 10^9 cc/mole-sec. This is several orders of magnitude greater than the corresponding reaction for alkyl radicals. This enhanced activity of the silyl radicals, considered in terms of the simple collision theory, can be related to: i) their greater physical size, though this is largely offset by the increased molecular weight in the expression for the collision number; ii) their larger polarizability which tends to increase the effective collision diameter; iii) their available d-orbitals which extend in all directions and minimize any steric hindrance associated with the reaction; iv) their geometry. Silyl radicals retain the tetrahedral molecular configuration and the unpaired electron possesses 22% s-character. The net energy required to rearrange the planar alkyl free radical and rehybridize the unpaired electron in the p atomic orbital to an sp^3 molecular orbital is not required in the case of the silyl radical thus the energy barrier for the addition reaction is lower. All of these factors increase the value of the expression for the rate constant.

Ethylene is an excellent trap for mono- and disilyl radicals.

TABLE III - XVII

Metathetical Reactions of Some Simple Alkyl Radicals with Disilane-d_6 and the Addition of Alkyl and Silyl Radicals to Olefins

Reaction	$\log k_{25°C}$ (cc/mole-sec)	Ref.
$CH_3 + Si_2D_6 \rightarrow CH_3D + Si_2D_5$	7.14	23
$C_2H_5 + Si_2D_6 \rightarrow C_2H_5D + Si_2D_5$	7.08	86
$n\text{-}C_3H_7 + Si_2D_6 \rightarrow n\text{-}C_3H_7D + Si_2D_5$	7.07	86
$Si_2D_5C_2H_4 + Si_2D_6 \rightarrow Si_2D_5C_2H_4D + Si_2D_5$	7.0	estimated
$CH_3 + C_2H_4 \rightarrow C_3H_7$	6.16	129
$CH_3 + C_3H_6 \rightarrow C_4H_9$	6.14	129
$C_2H_5 + C_2H_4 \rightarrow C_4H_9$	5.82	141
$n\text{-}C_3H_7 + C_2H_4 \rightarrow n\text{-}C_5H_{11}$	6.68	128
$Si_2D_5 + C_2H_4 \rightarrow Si_2D_5C_2H_4$	9.7	estimated[b]

TABLE III - XVII (cont'd)

Reaction	log $k_{25°C}$ (cc/mole-sec)	Ref.
$SiH_3 + C_3H_6 \rightarrow SiH_3C_3H_6$	9.89[a]	132

(a) Based on value of 10^{14} cc/mole-sec for k combination of SiH_3.

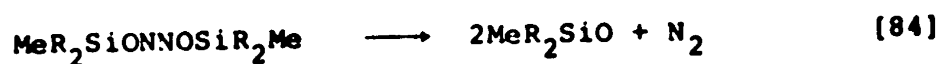
(b) Estimated from ratio $k_1/k_2 = 5 \times 10^2$.

d) Reactions with NO

The nature of the reactions between NO and silyl radicals is largely uncharacterized. Work instigated in this laboratory has shown that NO reacts with methyl substituted and monosilyl radicals, to form a siloxane in which the integrity of the primary radical is preserved (56,60-62). A radical derived by removal of a hydrogen atom from the substrate comprised the other substituent on the oxygen atom of the siloxane. In the case of the unsubstituted monosilyl radical, hydrogen, nitrogen and nitrous oxide all appeared as chain products. In the methylsilane plus nitric oxide system on the other hand, nitrous oxide was only a minor product compared to the hydrogen and nitrogen. Methane and ethylene became relatively more important as the concentration of nitric oxide was increased. All this led to the proposal of a tentative mechanism for the formation of nitrogen, hydrogen and siloxane in the methyl-substituted silane systems, viz.

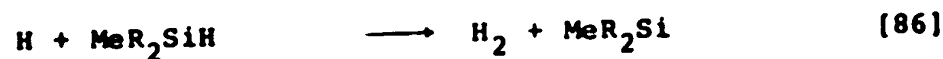
$$MeR_2Si + NO \longrightarrow MeR_2SiON \quad [82]$$

$$2MeR_2SiON \longrightarrow MeR_2SiONNOSiR_2Me \quad [83]$$



$$MeR_2SiONNOSiR_2Me \longrightarrow 2MeR_2SiO + N_2 \quad [84]$$

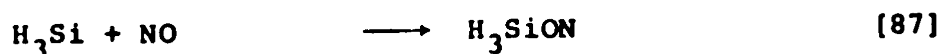
$$MeR_2SiO + MeR_2SiH \longrightarrow MeR_2SiOSiR_2Me + H \quad [85]$$



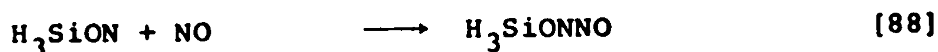
$$H + MeR_2SiH \longrightarrow H_2 + MeR_2Si \quad [86]$$

where R = (Me or H).

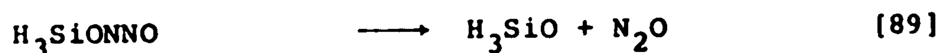
This mechanism has been revised somewhat by Kamaratos and Lampe (117) to account for the nitrous oxide found in the monosilane system.



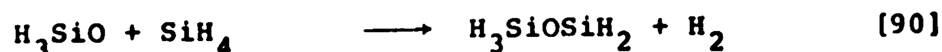
$$H_3Si + NO \longrightarrow H_3SiON \qquad [87]$$



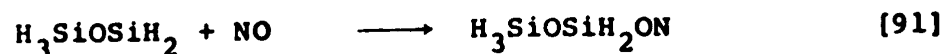
$$H_3SiON + NO \longrightarrow H_3SiONNO \qquad [88]$$



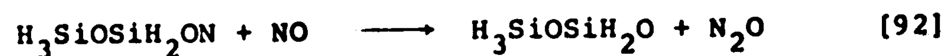
$$H_3SiONNO \longrightarrow H_3SiO + N_2O \qquad [89]$$



$$H_3SiO + SiH_4 \longrightarrow H_3SiOSiH_2 + H_2 \qquad [90]$$

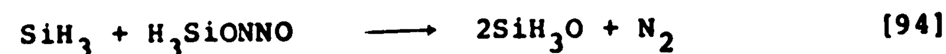


$$H_3SiOSiH_2 + NO \longrightarrow H_3SiOSiH_2ON \qquad [91]$$



$$H_3SiOSiH_2ON + NO \longrightarrow H_3SiOSiH_2O + N_2O \qquad [92]$$

$$H_3SiOSiH_2 + SiH_4 \longrightarrow H_3SiOSiH_3 + SiH_3 \qquad [93]$$

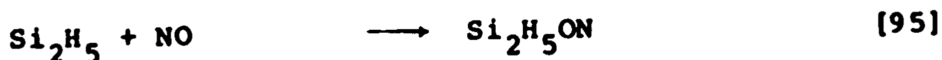


$$SiH_3 + H_3SiONNO \longrightarrow 2SiH_3O + N_2 \qquad [94]$$

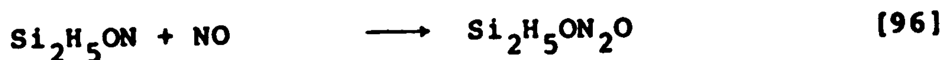
This mechanism predicts that N_2O and H_2 production rates are equal and that N_2 only becomes an important product when the concentration of NO is low enough that all of the silyl radicals are not scavenged. This is demonstrably not the case for the mercury sensitization of disilane (Table III-VI), where the N_2 yield was observed to increase as the initial NO concentration was increased. The enhancement of the N_2 yield was coupled with a rise in the total hydrogen recovered as a product. The yield of excess hydrogen as a function of initial NO pressure lagged the nitrogen and the nitrous

oxide, rose abruptly over the interval 2.5 to 4 torr and leveled off at a value approximately ½ of the N_2 yield. Simultaneously the N_2O began to decrease slightly and the more highly oxygenated siloxanes increased in importance.

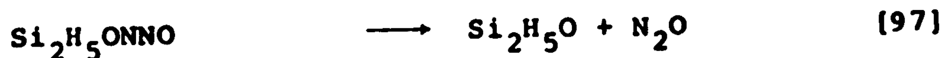
As pointed out in a recent comprehensive review of the role of NO in photochemistry (142) the adduct between alkyl radicals and NO in the presence of excess nitric oxide can act as a catalyst for the conversion of NO to $N_2 + NO_2$ or be removed by nitric oxide in a reaction which forms RO + N_2O. A modification of this is applied to the present system;



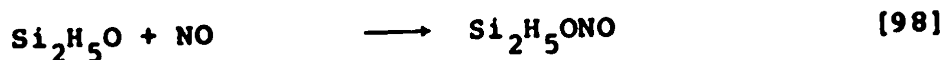
$Si_2H_5 + NO \longrightarrow Si_2H_5ON$ [95]



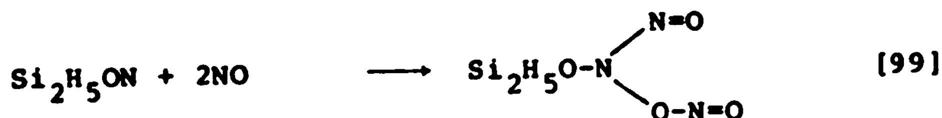
$Si_2H_5ON + NO \longrightarrow Si_2H_5ON_2O$ [96]

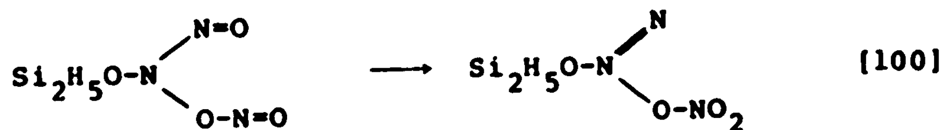


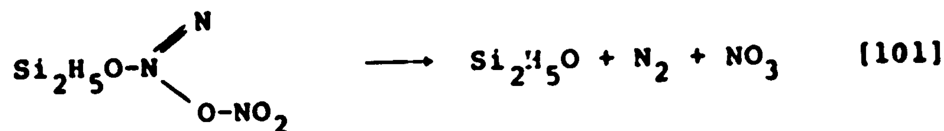
$Si_2H_5ONNO \longrightarrow Si_2H_5O + N_2O$ [97]



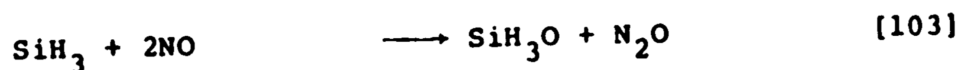
$Si_2H_5O + NO \longrightarrow Si_2H_5ONO$ [98]

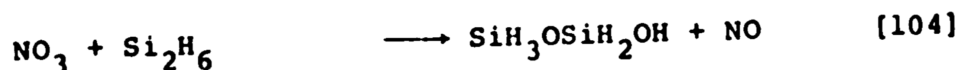


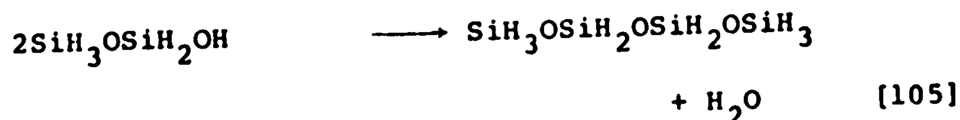


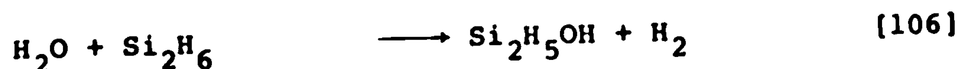


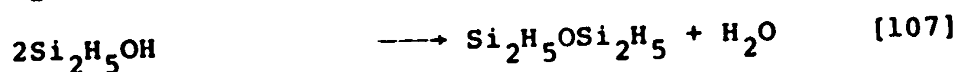
$Si_2H_5O + Si_2H_6 \longrightarrow Si_2H_5OSiH_3 + SiH_3$ [102]

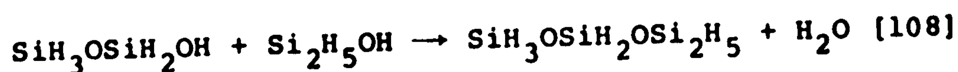


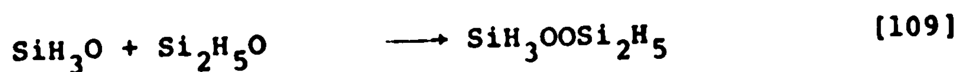




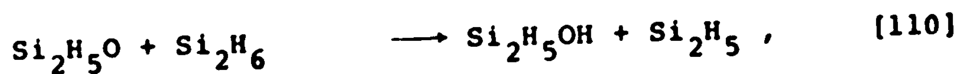








The silyl radicals are scavenged by the nitric oxide and transformed to siloxy radicals in [95]-[97]. The siloxy radicals may then either react further with NO, [98], or in the event of low NO concentration react with substrate and displace a silyl radical [102]. Another possible reaction would be abstraction of a hydrogen atom by the siloxy radical

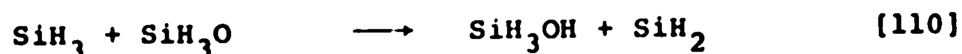


however the predominance of $Si_2H_5OSiH_3$ in the products at low [NO] suggests that this reaction is not important.

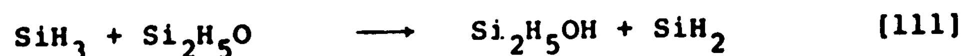
The NO_3 formed together with N_2 in the sequence [98]-[101] is postulated to oxidize the disilane substrate rather than react with NO to form $2NO_2$ as is the case in alkyl radical systems. Step [104] is speculative and the siloxysilanol if formed would be highly activated due

to the three new Si-O bonds in the molecule. This step provides a path for insertion of an oxygen atom into the Si-Si bond and the -Si-O-Si-O- linkages observed in the products. The known tendency of unsubstituted silanols to quantitatively condense to siloxanes as in [105], [107] and [108], results in a molecule of water. This leads to a molecule of hydrogen via [106] which will not co-produce monosilane. The suppressing effect on the monosilane yield through scavenging of the monosilyl radicals, is maintained since hydrogen is formed in a molecular elimination step.

The small yield of trisilane is maintained by minor chain terminating steps such as



$$SiH_3 + SiH_3O \longrightarrow SiH_3OH + SiH_2 \qquad [110]$$



$$SiH_3 + Si_2H_5O \longrightarrow Si_2H_5OH + SiH_2 \qquad [111]$$

followed by insertion of the silylene into the substrate.

The major chain terminating process [109] gives rise to an unstable silyl peroxide which can act as an oxidizing agent and is the unstable product which further oxidizes the siloxanes at room temperature.

3. Thermal Stability of Silyl Radicals

There was no previous information extant on the thermal stability of unsubstituted silyl radicals. The trimethyl silyl radical had been found to be more

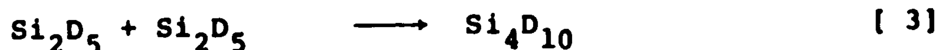
stable thermally than its hydrocarbon analogue, the t-butyl radical (56), in that no unimolecular decomposition occurred up to 400°C. The present results indicate that the radicals formed in the hydrogen plus disilane-d_6 and methyl plus disilane-d_6 systems do not decompose below 220°C. The following mechanism is proposed to account for the yield of products.

$$(CH_3)_2Hg + h\nu \longrightarrow 2CH_3 + Hg \qquad Ia$$

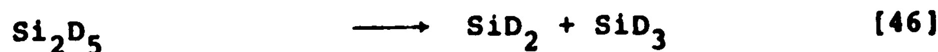
$$CH_3 + Si_2D_6 \longrightarrow CH_3D + Si_2D_5 \qquad [30]$$

$$CH_3 + Si_2D_5 \longrightarrow CH_3D + Si_2D_4 \qquad [31]$$

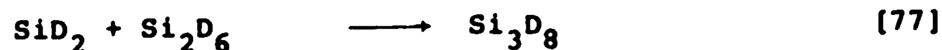
$$CH_3 + Si_2D_5 \longrightarrow CH_3SiD + SiD_4 \qquad [48]$$



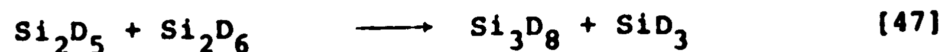
$$Si_2D_5 + Si_2D_5 \longrightarrow Si_4D_{10} \qquad [\ 3]$$



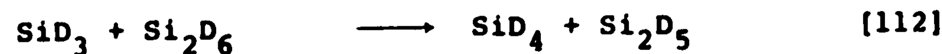
$$Si_2D_5 \longrightarrow SiD_2 + SiD_3 \qquad [46]$$



$$SiD_2 + Si_2D_6 \longrightarrow Si_3D_8 \qquad [77]$$



$$Si_2D_5 + Si_2D_6 \longrightarrow Si_3D_8 + SiD_3 \qquad [47]$$



$$SiD_3 + Si_2D_6 \longrightarrow SiD_4 + Si_2D_5 \qquad [112]$$

When reactions Ia, [30], [31], [47], [48] and [112] are considered the rate expressions are:

$$R_{SiD_4} = \frac{k_{48} Ia}{(k_{31}+k_{48})} + \frac{k_{47}\ k_{30}}{(k_{31}+k_{48})} [Si_2D_6]^2$$

$$R_{Si_3D_8} = \frac{k_{47}\ k_{30}}{(k_{31}+k_{48})} [Si_2D_6]^2$$

$$R_{Si_4D_{10}} = k_3 \left(\frac{k_{30}}{k_{31}+k_{48}}\right)^2 [Si_2D_6]^2 .$$

The monosilane-d_4 and trisilane-d_8 differ by a constant, provided k_{31} and k_{48} are both independent of temperature. The apparent activation energies listed in Table III-XVIII can be equated to definite steps i.e.

$$E_{Si_3D_8} = E_{47} + E_{30} - E_{31} = 8.4 \text{ kcal/mole}$$

and

$$E_{Si_4D_{10}} = E_3 + 2(E_{30} - E_{31}) = 2.5 \text{ kcal/mole.}$$

One can set $E_3 = 0$ and obtain $E_{30} - E_{31} = 1.25$ kcal/mole and from this a value for E_{47}, the displacement reaction between disilanyl radicals and substrate, of 7.1 kcal/mole. This value is not unreasonable since the enthalpy change for the reaction can be estimated as,

$$\Delta H_{47} = 26 + 50 - 55 - 17 = 4 \text{ kcal/mole.}$$

The value for $E_{30} - E_{31}$ is lower than the value of 7 kcal/mole found for the homogeneous activation energy of [30] though, and suggests that a heterogeneous component may be contributing to the reaction mechanism in the quartz cell.

A similar kinetic treatment of this mechanism in which [112] and [47] are replaced by [46] and [47] gives the following relations for the activation energies,

$$E_{Si_3D_8} = E_{46} + E_{30} - E_{31} = 8.4 \text{ kcal/mole}$$

$$E_{Si_4D_{10}} = E_3 + 2(E_{30}-E_{31}) = 2.5 \text{ kcal/mole.}$$

whence E_{46} = 7.1 kcal/mole. The enthalpy change for this reaction is

$$\Delta H_{46} = 50 + 53 - 55 = 48 \text{ kcal/mole,}$$

hence step [46] is not the rate determining step in this system. This is substantiated by the results from the H_2 plus Si_2D_6 system (Table III-XIV) where the tetra-silane would decrease and the mono- and trisilane species would increase if the disilanyl were decomposing.

Reaction [47] is a probable source of mono-silane and trisilane in the mercury sensitization of disilane at elevated temperatures but no reaction of monosilyl or disilanyl radicals observed in the CH_3 or H plus disilane-d_6 systems can explain the hydrogen, and the monosilane in excess of the trisilane (Table III-XII). The probability that this is due to Si_2H_5 being much more unstable than Si_2D_5 is low since it would entail a k_H/k_D ratio of 4 or 5 at 485°K. It is most probably associated with the reactions of hydrogen atoms with disilane at large substrate concentrations.

TABLE III - XVIII

Apparent Activation Energies in Kcal/mole for Formation of the Products from $CH_3 + Si_2D_6$ and $Hg^* + Si_2H_6$

	PRODUCT			
System	Hydrogen	Monosilane	Trisilane	Tetrasilane
$Hg^* + Si_2H_6$				
Low Temperature	0.23 ± 0.18	1.44 ± 0.32	2.84 ± 0.18	0.10 ± 0.3
High Temperature	8.64	11.2	10.8	3.96
$CH_3 + Si_2D_6$	-	a	8.4 ± 0.5	2.5 ± 0.2

(a) Not measured.

CHAPTER IV

The Mercury Photosensitized Decomposition of Phenylsilane

RESULTS

Preliminary investigation showed that phenylsilane-d_3 underwent no thermal decomposition in two hours at 175°C. Photosensitized decomposition occurred at room temperature as well as at higher temperatures. The reaction was studied most extensively at 105°C and to a lesser extent at 60 and 166°C.

The data in Table IV-I show the effect of pressure on the quantum yields of D_2, SiH_4, ϕ-D and ϕ-Si_2D_5 at 105°C. The non-variation of the quantum yields of D_2, ϕ-D and ϕ-Si_2D_5 with pressure shows that complete quenching of the excited mercury atoms was occurring over the entire pressure range. The decrease in the quantum yield of monosilane at low pressure indicated that the isotopically pure SiD_4 was probably formed by abstraction of a deuterium atom from the side chain by a SiD_3 radical.

The enhanced SiD_4/D_2 ratio for one hour irradiation times was taken as evidence for either a buildup in concentration of some uncharacterized source of readily abstractable deuterium atoms or the secondary decomposition of some, again uncharacterized,

TABLE IV - I

Photosensitization of ϕ-SiD_3 for an Irradiation Time of 10 minutes as a Function of Pressure, at 105±2°C

ϕ-SiD_3 Pressure Torr	I_a μeinsteins/min before	after	ϕ, moles/einstein D_2	SiD_4	ϕ-D	ϕ-Si_2D_5	SiD_4/D_2
9.4	0.244	0.196	0.15	0.21	0.051	0.032	1.4
11.0	0.189	0.186	0.22	0.23	0.063	0.039	1.0
13.0	0.202	0.189	-	0.16	-	-	-
47.0	0.258	0.228	0.26	0.35	0.027	0.028	1.3
50.0	0.183	0.183	0.27	0.42	-	-	1.6
51.0	0.302	0.252	0.20	0.45	-	-	2.2
52.0	0.262	0.228	0.24	0.47	0.054	0.041	2.0
56.0	0.242	0.246	0.37	0.50	-	-	1.4
58.0	0.230	0.151	0.35	0.43	-	-	1.2
59.0	0.178	0.169	0.31	0.43	0.068	0.036	1.4
60.0	0.210	0.187	0.16	0.60	-	-	3.8
61.0	0.246	0.242	0.23	0.40	-	-	1.7
63.0	0.208	0.198	0.20	0.32	0.068	0.021	1.6
68.0	0.242	0.208	0.22	0.45	-	-	2.0
92.0	0.188	0.184	0.31	0.59	-	-	1.9
93.0	0.166	0.166	0.39	0.71	0.10	0.054	1.8
97.0	0.184	0.166	0.26	0.46	0.064	0.042	1.8
128	0.218	0.218	0.22	0.40	0.070	0.046	1.8
165	0.218	0.198	0.24	0.37	0.065	0.043	1.5
280	0.198	0.202	0.28	0.60	-	-	2.1
11.2[a]	0.317	0.175	0.10	0.10	-	-	1.0
61.4[a]	0.284	0.167	0.16	-	-	-	-
65.2[a]	0.317	0.246	0.06	0.20	-	-	3.3
68.5[a]	0.300	0.160	0.13	0.33	-	-	2.5
157[a]	0.274	0.169	0.13	0.49	-	-	3.8

[a] Photolysis time of 60 minutes.

TABLE IV - II

Effect of Temperature on Quantum Yields for the Photosensitization of Phenylsilane, d_3 for 10 minutes

Temperature	I_a μeinsteins/min		ϕ-SiD_3 Concentration	Φ, moles/Einstein				SiD_4/D_2
°C	before	after	moles/liter$\times 10^3$	D_2	SiD_4	ϕ-D	ϕ-Si_2D_5	
60	0.264	0.254	2.37	0.14	0.13	0.049	0.035	0.93
60	0.254	0.229	2.27	0.17	0.16	0.048	0.031	0.94
62	0.286	0.230	2.38	0.26	0.19	-	-	0.73
62	0.264	0.202	2.36	0.21	0.14	0.070	0.031	0.67
62	0.230	0.190	2.14	0.17	0.14	0.058	0.025	0.82
103	0.302	0.252	2.24	0.20	0.38	-	-	1.9
105	0.258	0.228	2.08	0.26	0.35	0.027	0.028	1.3
105	0.183	0.183	2.23	0.27	0.42	-	-	1.6
105	0.262	0.228	2.28	0.24	0.47	0.054	0.041	2.0
166	0.224	0.224	2.07	0.22	1.00	0.040	0.029	4.5
166	0.233	0.230	1.96	0.15	0.68	0.033	0.014	4.5
166	0.227	0.234	1.93	0.14	0.47	0.018	0.004	3.4

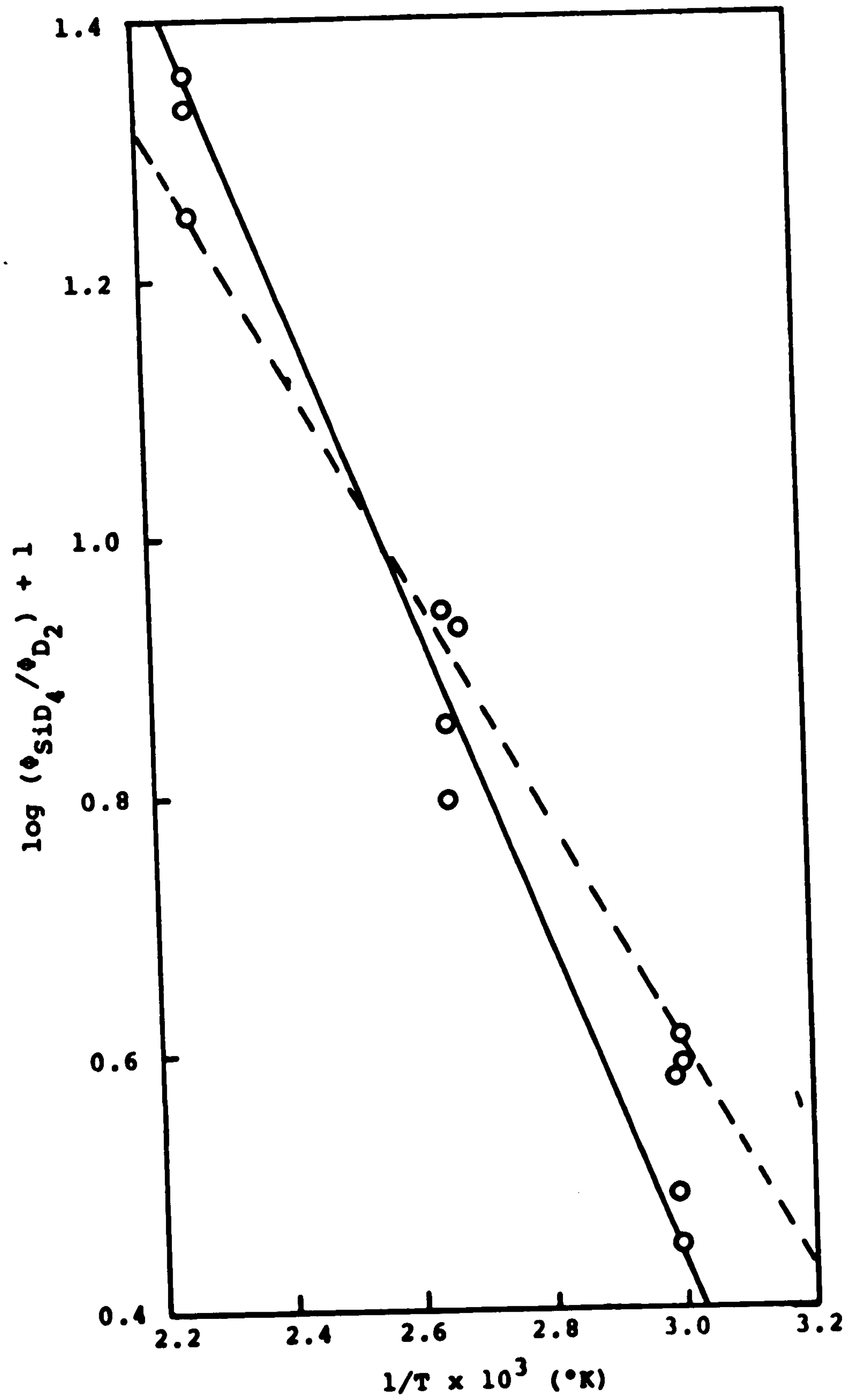


FIGURE IV-1: Arrhenius plot of Φ_{SiD_4}/Φ_{D_2} for ϕ-SiD_3.

source of silyl radicals.

The variation of the same four product yields with temperature is presented in Table IV-II. The data show that the only product which varied significantly with temperature was monosilane and it increased as the temperature was elevated. The scatter in the SiD_4/D_2 ratio is not as great as it is for monosilane and when log (SiD_4/D_2) is plotted versus the reciprocal of the absolute temperature the apparent activation energy difference lies between 5.8 and 4.0 kcal/mole (Figure IV-1).

The quantum yield of D_2 remained constant within experimental error over the 100° range. Three plausible explanations for this phenomenon were considered; 1) molecular elimination of D_2 in a primary step, 2) $\Phi_D \approx 0.25$, and unit efficiency for the metathetical reaction between the atoms and the $-SiD_3$ side chain, or 3) $\Phi_D \approx 1$, and a constant ratio for the rate constants for the metathetical reaction and the expected addition to the phenyl ring, i.e. $k_{metathesis}/k_{addition} \approx 1/3$, over the entire temperature range.

The first postulate was tested by photosensitizing various ratios of phenylsilane and phenylsilane-d_3. The results are given in Table IV-III and they showed that HD was an important product in the mixture, thus molecular elimination was not the only mode of forming

TABLE IV - III

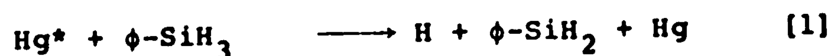
Isotopic Composition of Hydrogen Found in the Photosensitization of ϕ-SiD_3 + ϕ-SiH_3 at 110°C for 10 Minutes Irradiations

Total Pressure Torr	ϕ-SiH_3 %	Hydrogen %			Hydrogen % Corrected for Isotopic Impurity of Substrate (a)		
		H_2	HD	D_2	H_2	HD	D_2
51.8	0	3.2	8.3	88.4	0	0	100
65.3	16.9	8.9	34.4	56.7	7.5	31.2	61.3
53.6	42.8	29.8	45.8	24.4	26.9	45.0	28.1
56.2	64.1	52.2	38.4	9.4	49.7	39.7	10.6
53.6	80.4	73.3	23.8	2.9	71.6	24.9	3.5
51.4	100	99.2	0.74	0.05	100	0	0

(a) Derivation given in Appendix C

D_2. The contribution of the molecular step can be evaluated from the data in the following manner. When the possibility for both molecular and atomic formation is included in the primary step the hydrogen producing mechanism is,

$$Hg + h\nu \xrightarrow{\lambda=253.7nm} Hg^* \qquad \text{Ia}$$



$$Hg^* + \phi\text{-}SiH_3 \longrightarrow H + \phi\text{-}SiH_2 + Hg \qquad [1]$$

$$\longrightarrow H_2 + \phi\text{-}SiH + Hg \qquad [2]$$

$$Hg^* + \phi\text{-}SiD_3 \longrightarrow D + \phi\text{-}SiD_2 + Hg \qquad [3]$$

$$\longrightarrow D_2 + \phi\text{-}SiD + Hg \qquad [4]$$

$$H + \phi\text{-}SiH_3 \longrightarrow H_2 + \phi\text{-}SiH_2 \qquad [5]$$

$$+ \phi\text{-}SiD_3 \longrightarrow HD + \phi\text{-}SiD_2 \qquad [6]$$

$$D + \phi\text{-}SiH_3 \longrightarrow HD + \phi\text{-}SiH_2 \qquad [7]$$

$$+ \phi\text{-}SiD_3 \longrightarrow D_2 + \phi\text{-}SiD_2 \qquad [8]$$

Steady-state treatment of this scheme yields the relation,

$$\frac{X_{D_2}}{X_{HE}} = \left(k_4 + \frac{k_8 k_3 [HE]}{k_7 [LI] + k_8 [HE]}\right) \left(\frac{[HE]+[LI]}{(k_1+k_2)[LI]+(k_3+k_4)[HE]}\right)$$

which reduces to

$$\frac{X_{D_2}}{X_{HE}} = \frac{k_4}{k_1+k_2} \quad \text{at the limit } [HE] \rightarrow 0;$$

where X_{D_2} = mole fraction of D_2 in the total hydrogen product

X_{HE} = mole fraction of $C_6H_5SiD_3$ in the reaction mixture

[HE] = concentration of $C_6H_5SiD_3$

[LI] = concentration of $C_6H_5SiH_3$.

This relation is plotted in Figure IV-2 and the extrapolation value for $k_4/(k_1+k_2)$ is 0.08. Steps [2] and [4] can therefore be neglected as sources of molecular hydrogen and deuterium. Two more useful relationships can be derived (Appendix C) and evaluated from the data. They are plotted in Figure IV-3 and give,

$$\frac{X_{HD}}{X_{HE}} \quad [HE] \to 0 = \frac{k_6}{k_5} \quad \frac{k_1}{k_1+k_2} + \frac{k_3}{k_1+k_2} = 1.36$$

$$\frac{X_{HD}}{X_{LI}} \quad [LI] \to 0 = \frac{k_7}{k_8} \quad \frac{k_3}{k_3+k_4} + \frac{k_1}{k_3+k_4} = 2.46$$

It has just been shown that $\frac{k_1}{k_1+k_2} = \frac{k_3}{k_3+k_4} = 1$ so the above equations simplify to

$$\frac{k_6}{k_5} + \frac{k_3}{k_1+k_2} = 1.36$$

$$\frac{k_7}{k_8} + \frac{k_1}{k_3+k_4} = 2.46.$$

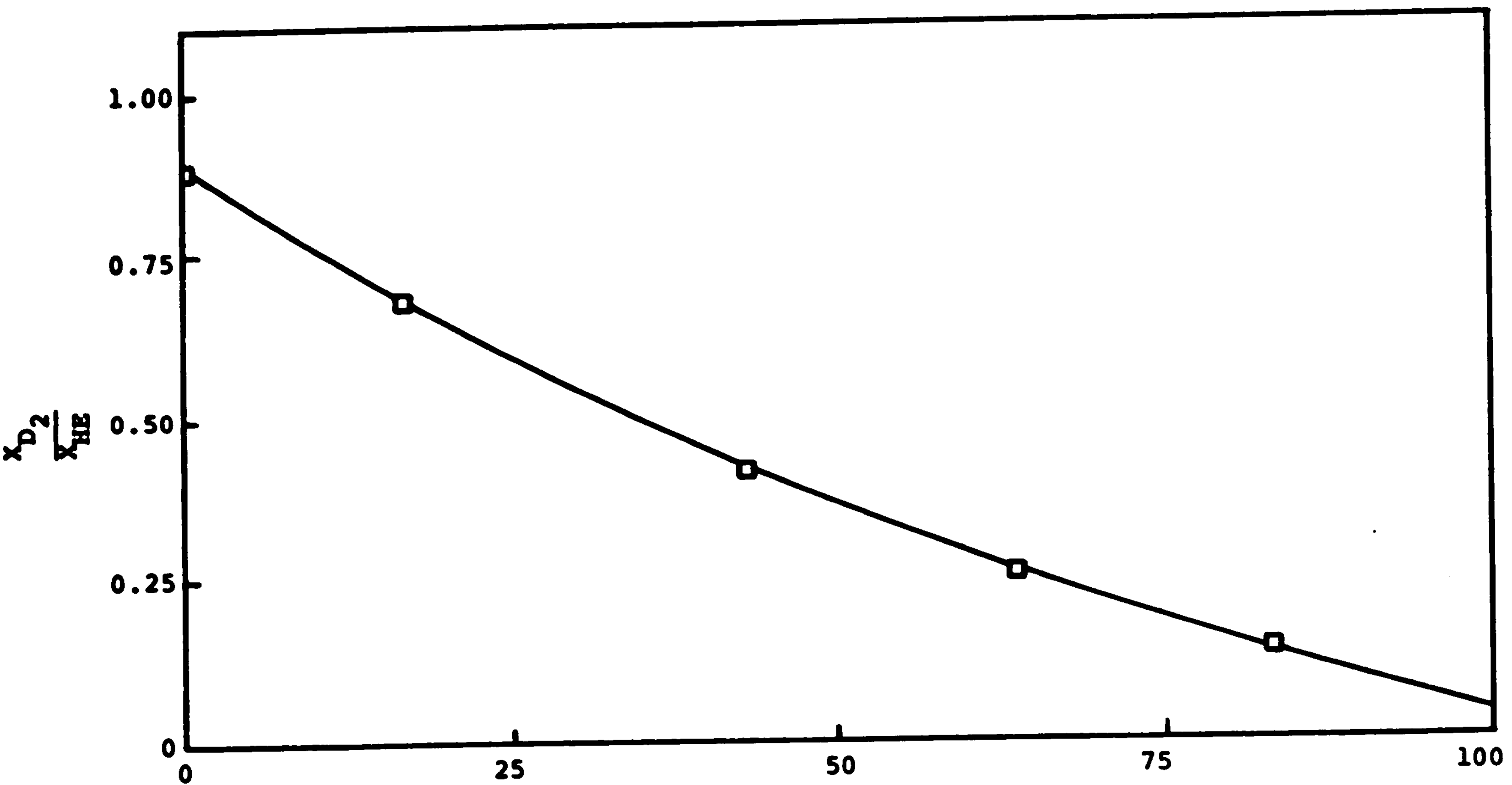


FIGURE IV-2: Variation of the mole fraction of D_2 with the mole fraction of ϕ-SiD_3 as a function of the composition of a mixture of ϕ-SiH_3 and ϕ-SiD_3 at 110°C.

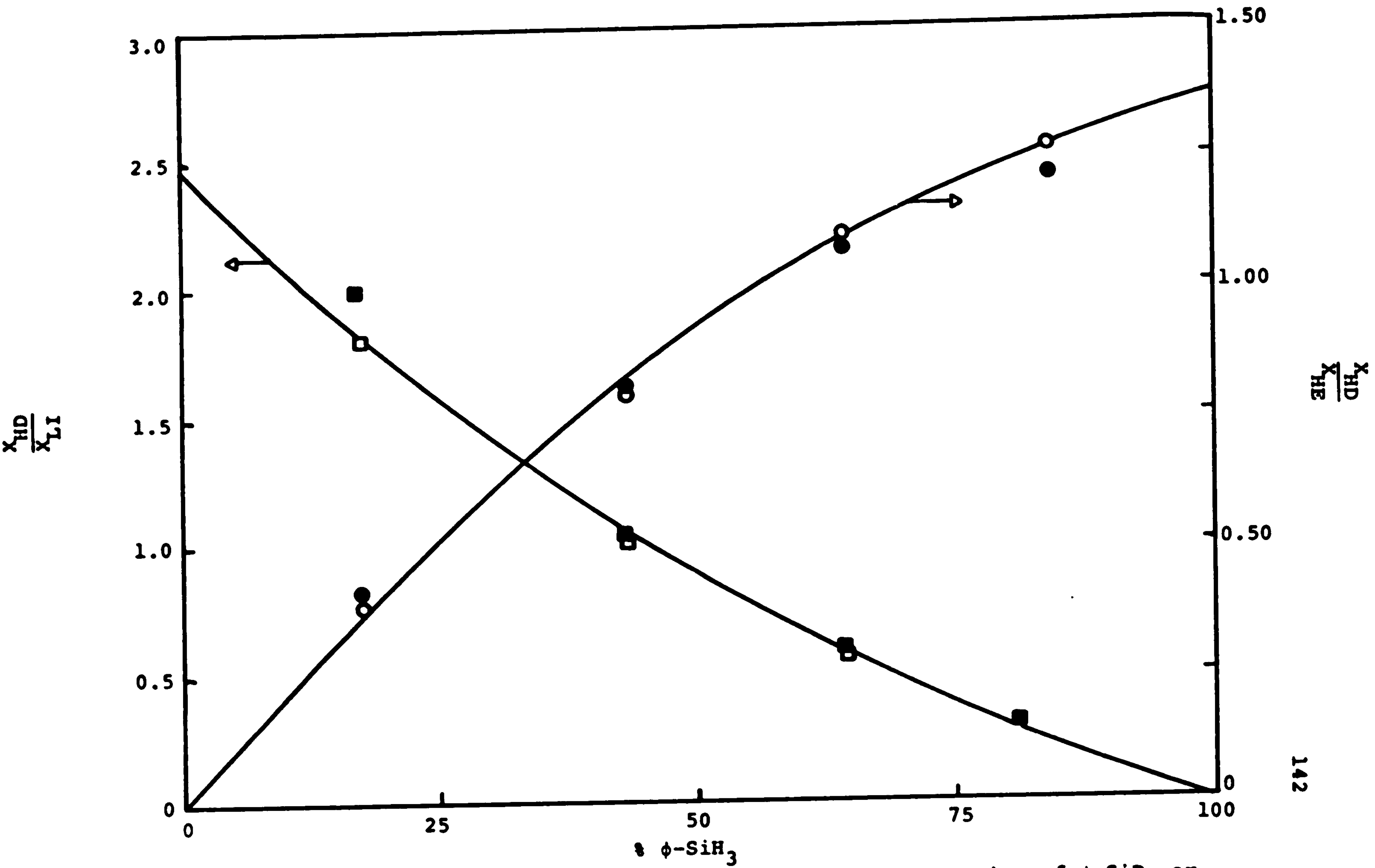


FIGURE IV-3: Variation of the mole fraction of HD with the mole fraction of ϕ-SiD_3 or ϕ-SiH_3 as a function of the composition of a mixture of ϕ-SiD_3 and ϕ-SiH_3 at 110°C.

The assumption was made that quenching by the silicon deuterium bond was responsible for the formation of the atoms. This is a reasonable assumption since no decrease in the hydrogen yield by increased pressure was observed as might be expected if the excited phenyl ring was eliminating a β-hydrogen (Table IV-I). Then, because deuteration of methylsilane was found to have no effect on the primary quenching process (56), and in an auxiliary study the ratio k_9/k_{10} for

$$Hg^* + SiH_4 \rightarrow \text{products} + Hg \qquad [9]$$

$$Hg^* + SiD_4 \rightarrow \text{products} + Hg \qquad [10]$$

was found to be unity (143), the following was also true,

$$\frac{k_3}{k_1+k_2} = \frac{k_1}{k_3+k_4} = 1.$$

We now have evaluated the k_H/k_D isotope effect for the abstraction by both hydrogen and deuterium atoms:

$$\frac{k_5}{k_6} = 2.78 \text{ at } 110°C$$

and $$\frac{k_7}{k_8} = 1.46 \text{ at } 110°C.$$

Returning now to postulates 2) and 3) for the invariant hydrogen yield, these were tested by producing hydrogen atoms in the presence of phenylsilane and phenylsilane-d_3 under varying conditions of pressure

and temperature. The yield of HD in the large excess of H_2 could not be monitored but the monosilane yield could be. It was known that ϕ-SiH_2 radicals displace SiH_3 from phenylsilane (70) and the present work had shown that the monosilane yield increased with increasing pressure at a constant temperature and also increased with increasing temperature at a constant pressure. Thus it was reasoned that if postulate 2) were operative the quantum yield of monosilane should approach the quantum yield of hydrogen atoms at high enough pressure and/or temperature. The results are given in Table IV-IV and while ΦSiD_4 does increase with temperature and with pressure it doesn't approach the quantum yield of hydrogen atoms, $\Phi H = 2$ (127). Postulate 2) was revoked in favour of 3).

Postulate 3) receives further support from the data in Table IV-V. The quantum yield of SiH_4 from the photosensitization of phenylsilane is greater than that for SiD_4 from the photosensitization of phenylsilane-d_3, all other things being equal. This reflects the primary isotope effect for the metathesis between silyl radicals and the silyl side chain of the aromatic molecule.

The magnitude of ΦD in postulate 3) remains to be determined. In view of the large quenching cross section of the aromatic ring (121), quenching at the hydridic silicon-deuterium bond should have less than unit efficiency. This was indicated when NO was added to

TABLE IV - IV

Quantum Yields of Monosilane and Benzene from the 10 Minute Reaction of Hydrogen Atoms with Phenylsilane

Phenylsilane Pressure Torr	Hydrogen Pressure Torr	I_a μeinsteins/min before	after	Temperature °C	Φ, Moles/Einstein Monosilane	Benzene
3.0	300	0.248	0.248	25	0.023	0.071
3.6	360	0.248	0.232	25	-	0.060
4.8	480	0.232	0.240	25	0.034	0.064
7.8	780	0.240	0.242	25	0.045	0.058
9.2	920	0.242	0.242	25	0.048	0.049
4.0	506	0.272	0.202	165	0.134	0.042
4.0	457	0.202	0.148	165	0.220	0.040
50.5[(a)]	496	0.195	0.143	110	0.94	<0.1
50.5[(a)]	510	0.195	0.118	110	0.97	<0.1
42.0[(a)]	598[(b)]	0.118	0.110	110	0.98	<0.1

(a) Pressure of ϕ-SiH_3; (b) Pressure of D_2.

TABLE IV - V

Effect of Isotopic Composition and Photolysis Time on Ratio of Monosilane to Hydrogen in the Photosensitization of Phenylsilane at 110°C

Total Pressure Torr	ϕ-SiH_3 %	Time min	Products µmoles		ϕ, Moles/Einstein		Monosilane / Hydrogen
			Hydrogen	Monosilane	Hydrogen	Monosilane	
50.0	0	10	0.48	0.76	0.27	0.42	1.6
52.3	0	10	0.34	-	-	-	-
51.8	0	12	0.38	0.74	-	-	1.9
65.3	16.9	18	0.52	1.28	-	-	2.5
53.6	42.8	23	0.66	1.91	-	-	2.9
52.6	60.6	16	0.41	1.48	-	-	3.6
56.2	64.1	18	0.37	1.91	-	-	5.1
53.6	80.4	18	0.33	1.56	-	-	4.7
51.4	100	33	0.54	3.90	-	-	7.2
51.0	100	10	0.46	1.54	0.22	0.75	3.4
54.0	100	10	0.50	1.87	0.20	0.75	3.8

the sensitization system to delineate the mono-radical reactions form any molecular or biradical processes. The results given in Table IV-VI show that the monosilane yield was eliminated but that benzene and phenyldisilane were not completely suppressed by the radical scavenger. An electronically excited state of phenylsilane-d_3 could undergo silylene elimination to form a molecule of benzene-d_1 and the unscavengable silylene would then insert into a silicon-hydrogen bond of phenylsilane.

The presence of diphenylsilane was verified through a modification of the analytical procedure. An aliquot of the entire reaction mixture after photosensitization was subjected to mass spectral analysis. Mass to charge ratios corresponding to the molecular weights of $(\phi)_2$ and $(\phi\text{-}SiD_2)_2$ were observed as well as that corresponding to ϕ_2SiD_2. A semiquantative calculation estimated the relative importance of the above products relative to monosilane as; $SiD_4 \sim \phi_2SiD_2 >> \phi_2$, $(\phi SiD_2)_2$.

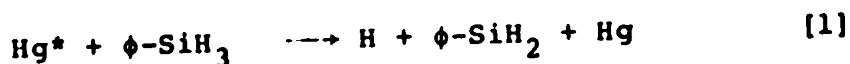
DISCUSSION

The foregoing results indicate that the mercury photosensitization of phenylsilane or phenylsilane-d_3 results in unit decomposition of the molecule. The main mode of primary decomposition is silicon-hydrogen bond cleavage

TABLE IV - VI

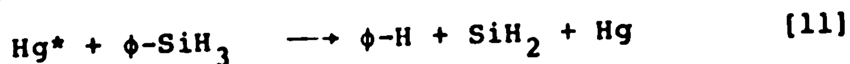
Effect of NO on the Product Yields from the Photosensitization of 18 torr of ϕ-SiD_3 at Room Temperature

Time Minutes	NO Pressure Torr	Product Yield, μmoles					
		D_2	N_2+D_2	N_2O	SiD_4	ϕ-D	ϕ-Si_2D_5
10	0	0.36	-	-	0.90	0.050	trace
10	1.0	-	0.88	3.1	0.00	0.036	trace
13	1.3	-	0.95	3.7	0.00	0.028	trace

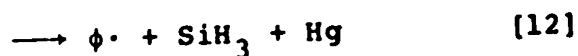


$$Hg^* + \phi\text{-}SiH_3 \longrightarrow H + \phi\text{-}SiH_2 + Hg \qquad [1]$$

Two other primary decomposition processes appear to be operative,



$$Hg^* + \phi\text{-}SiH_3 \longrightarrow \phi\text{-}H + SiH_2 + Hg \qquad [11]$$



$$\longrightarrow \phi\cdot + SiH_3 + Hg \qquad [12]$$

Reaction [11] is supported by the observation that its quantum yield is constant over the various conditions used and also by the fact that when nitric oxide was added to the system the yields of benzene and diphenylsilane were not eliminated. The detection of biphenyl as a reaction product leads to the proposal that [12] is one of the primary decomposition steps. In a separate study of the mercury sensitized decomposition of phenylsilane in a fast-flow system coupled to the ion source of a mass spectrometer it was also concluded that Si-D bond rupture was the major decomposition process (115). Attempts to measure the importance of [12] by trapping the phenyl radicals produced with methyl,

$$\phi\cdot + CH_3 \longrightarrow \phi\text{-}CH_3,$$

indicated that approximately 5 to 6% of the phenylsilane decomposed terminated as toluene. Combining this data with the results obtained in this study, the importance of the primary decomposition processes are estimated to be,

$\Phi_{[1]} \geq 0.80$

$\Phi_{[11]} \simeq 0.10$

$\Phi_{[12]} \leq 0.10.$

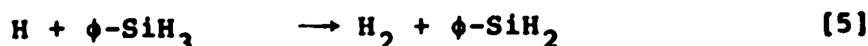
These results contrast markedly with those found for toluene where no decomposition was observed on photosensitization at room temperature and the quantum yield of hydrogen was only 0.1 at 400°C (144). In the case of the aromatic hydrocarbons the decomposition was found to be via an excited molecule formed in the initial quenching step since the yield of product passed through a maximum with pressure (144-146).

The fact that the 112 kcal/mole transferred to the hydrocarbon by the excited mercury atom was not effective in cleaving the benzylic carbon-hydrogen bond suggests that a photophysical process (phosphorescence) (147) was dissipating the energy before it could accumulate in that bond.

Since the benzylic carbon-hydrogen bond in toluene is only 85 kcal/mole (137) and the Si-H bond in phenylsilane is approximately the same as the 94 kcal/mole Si-H bond in monosilane (23), the difference in the decomposition of toluene and phenylsilane cannot be ascribed to the lower bond energy in the silane. This leaves two possibilities; 1) nearly 80% of the primary quenching is

done by the hydridic Si-H linkage, or 2) the silyl side chain so alters the energy surfaces reached by the excited phenyl group that efficient energy transfer to the side chain is occurring before pressure induced relaxation can take place. Sufficient information is not available to choose between these alternatives.

Within the proposed reaction scheme approximately 30% of the hydrogen atoms produced in step [1] abstract from the silyl side chain to form hydrogen molecules and the remainder add to the phenyl ring (148, 149):



$$H + \phi\text{-}SiH_3 \longrightarrow H_2 + \phi\text{-}SiH_2 \quad [5]$$

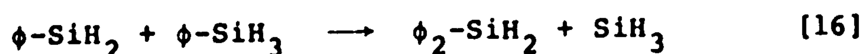
[13]

The most probable fate of the substituted cyclohexadienyl radical formed in step [13] is combination or disproportionation with another radical or further addition to substrate molecules to form a high molecular weight compound (150):

[14]

[15]

As mentioned above phenylsilyl radicals are capable of displacing silyl from a substrate molecule (70),



$$\phi\text{-}SiH_2 + \phi\text{-}SiH_3 \longrightarrow \phi_2\text{-}SiH_2 + SiH_3 \qquad [16]$$

Thus the phenylsilyl radicals formed in reactions [1] and [5] act as a source of silyl. It is most probably reaction [16] which has the positive temperature coefficient associated with it and which is responsible for the apparent activation energy of 6 kcal/mole as determined from the slope of the line in Figure IV-1. At lower temperatures the phenylsilyl radicals will terminate as the dimer

$$2\phi\text{-}SiH_2 \longrightarrow \phi\text{-}SiH_2SiH_2\text{-}\phi \qquad [17]$$

or disproportionate with the cyclohexadienyl radical, step [14].

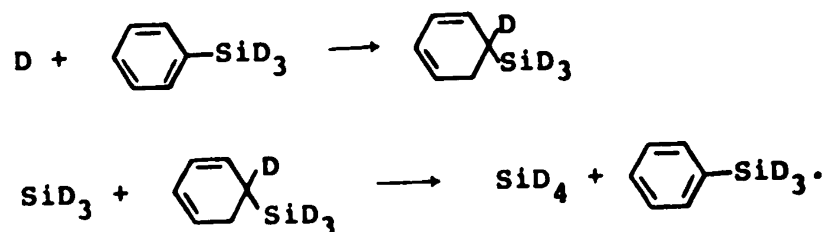
Silyl from both the primary step and the displacement reaction abstract from the silyl side chain,

$$SiH_3 + \phi\text{-}SiH_3 \longrightarrow SiH_4 + \phi\text{-}SiH_2 \qquad [18]$$

As mentioned in the previous section reaction [18] is most probably thermoneutral (23). In hydrocarbons, thermoneutral hydrogen atom transfer reactions are normally associated with activation energies of 12 kcal/mole or greater (91). An activation energy of this magnitude in the phenylsilane system would render reaction [18] an improbable source of monosilane. The observation that it is a source of SiH_4 is supported by the study of the reactions of isopropyl radicals with monosilane.

It was found that the activation energy for hydrogen atom abstraction from monosilane was 7.6 kcal/mole (86). This is an example of a thermoneutral metathetical reaction with a relatively low activation energy requirement.

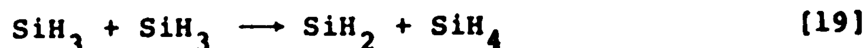
An alternative path for monosilane production involving the disproportionation of monosilyl with cyclohexadienyl radicals was also considered. Because of the fact that the monosilane product was exclusively SiD_4 when ϕ-SiD_3 was decomposed, a mechanism whereby only D atoms could be involved was required. The following process was thought to be a possible solution,



This scheme was tested using the photosensitized decomposition of D_2 in the presence of 10% ϕ-SiH_3. If the above reactions were occurring the isotopic composition of the monosilane product would be SiH_3D. Mass spectral analyses of the monosilane showed that it was solely SiH_4 thereby ruling out the disproportionation sequence and lending further weight to the abstraction reaction [18].

The absence of disilane as a reaction product is in agreement with the results involving H atoms and

SiD_4 + SiH_4 (Chapter III) where the disilane was d_0, d_2, d_4 or d_6, and the reaction of recoil silicon atoms with phosphine (151). The recoil atoms are reported to react with gaseous phosphine to give only SiH_4 as a product. When SiH_4 was introduced into the reaction system, Si_2H_6 became an important product. The observation that the radical scavengers NO and C_2H_4 had little or no effect on the Si_2H_6 yield led the authors to suggest that SiH_2 was the disilane precursor. Any silylene atom formed by disproportionation of the silyl radicals



$$SiH_3 + SiH_3 \longrightarrow SiH_2 + SiH_4 \qquad [19]$$

or from reaction [11] will insert in a silicon-hydrogen bond of the phenylsilane to produce phenyldisilane.

In conclusion mercury photosensitization of phenylsilane did prove to be a source of monosilyl radicals. They differ in their reactions from the alkyl-substituted silyl radicals in that self-disproportionation occurs to the exclusion of combination. The primary step in the photosensitization of the aromatic-substituted silicon hydride resembles the primary step in alkyl-substituted silicon hydrides and the paraffin hydrocarbons more than the primary step in the mercury photosensitization of unsaturated hydrocarbons. It was estimated that 80% of the primary quenching resulted in Si-H bond cleavage. The 20% which occurred at the π-system gave

decomposition products which were independent of the total pressure in the reaction vessel.

CHAPTER V

The Near-Ultraviolet Photolysis of Disilane

RESULTS

Disilane was photolyzed through 15 cm of air with the full arc of the medium pressure mercury lamp. The only effective emission lines were those at 194, 197 and 200 nm since the next emission line, at 225 nm, lies above the onset of absorption (Figure V-1). The products of the photolysis in decreasing order of abundance were H_2, SiH_4, Si_3H_8, n-Si_4H_{10}, i-Si_4H_{10} and a solid polymer on the cell walls. The polymer attenuated the incident light intensity but was observed not to produce products in the empty reaction vessel when exposed to actinic light.

The effect of time on the product yields was studied to differentiate between products of primary and secondary origin. The results are given in Table V-I. A plot of the product mole-fractions versus exposure time (Figure V-2) shows that H_2, SiH_4, Si_3H_8 and Si_4H_{10} all extrapolate to finite values at zero exposure time indicating that they are of primary origin. The observed increase of hydrogen and monosilane fractional yields at longer exposure times is a result of secondary photolysis

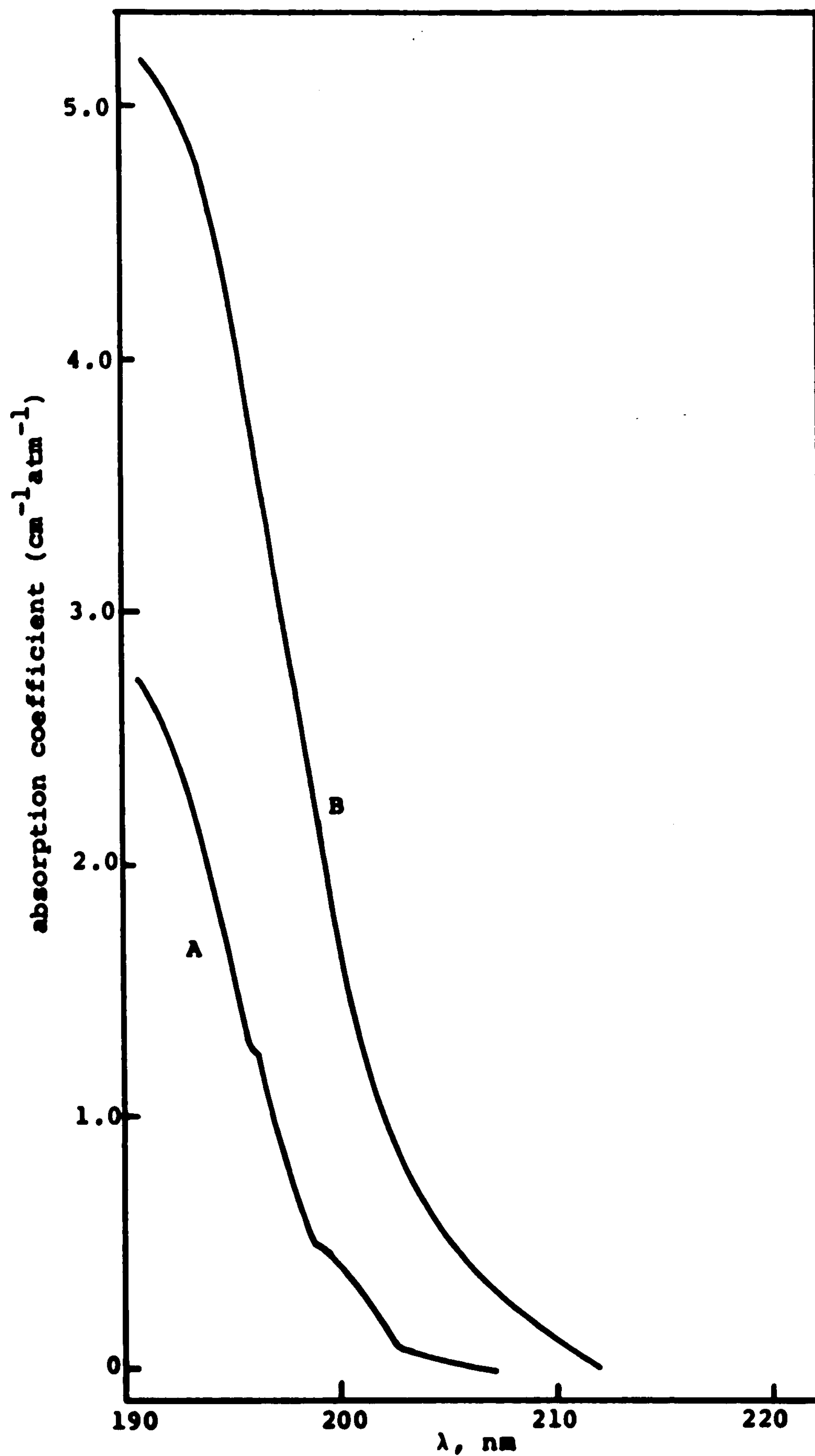


FIGURE V-1: Absorption spectrum of Si_2H_6 and Si_2D_6

A, Si_2D_6; B, Si_2H_6

TABLE V - I

Effect of Exposure Time on the Product Yields from the Photolysis of 100 Torr of Si_2H_6 at Room Temperature

Time Minutes	Products, μmoles			
	H_2	SiH_4	Si_3H_8	Si_4H_{10}
2	1.00	0.85	0.86	0.14
5	2.00	1.65	1.68	0.22
9	3.20	2.70	2.52	0.28
14	4.39	3.78	3.14	0.33

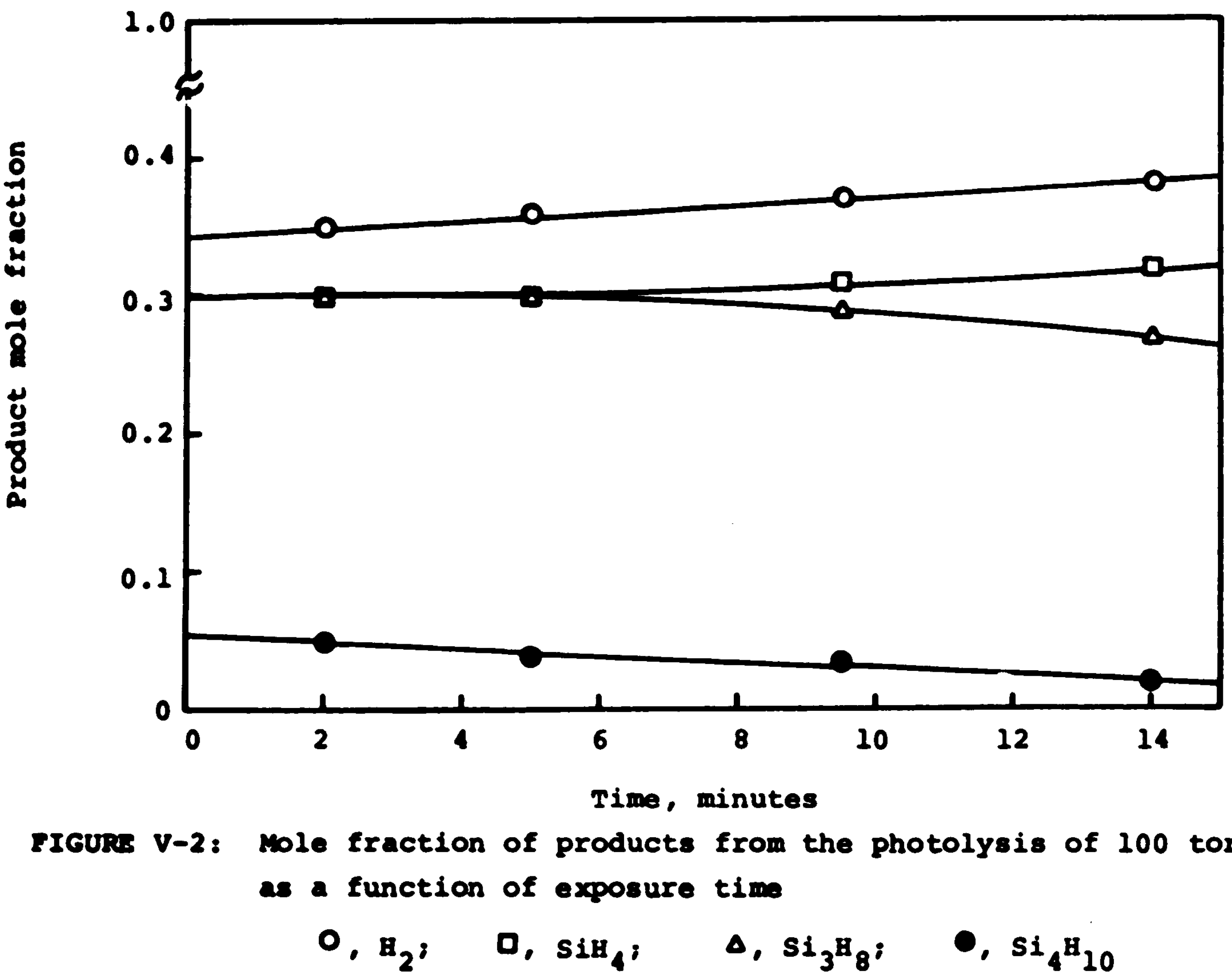


FIGURE V-2: Mole fraction of products from the photolysis of 100 torr Si_2H_6 as a function of exposure time

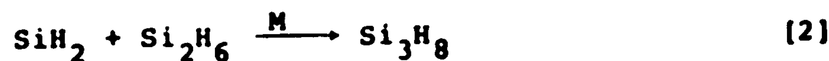
○, H_2; □, SiH_4; △, Si_3H_8; ●, Si_4H_{10}

of tri- and tetrasilane. The onset of absorption of these compounds is red-shifted from that of disilane (2c, 152). There is a wealth of lines in the emission spectrum of the lamp above 225 nm. Overlap of the absorption spectrum of these products and the emission spectrum can lead to significant secondary photolysis of the Si_3H_8 and Si_4H_{10}.

The effect of pressure on the product yields was studied next. The results are given in Table V-II. Complete absorption of the incident radiation was realized at pressures greater than ca 100 torr, as evidenced by the invariant total product yield. The mole fractions of H_2, SiH_4, Si_3H_8 and Si_4H_{10} are plotted in Figure V-3. There are two distinct regions on the graph. Above 30 torr the fractional yields are constant; below this pressure the hydrogen and monosilane increase as the tri- and tetrasilane decrease indicating that the latter were formed in vibrationally excited states which decomposed to hydrogen and monosilane unless pressure stabilized.

The observation that the monosilane and trisilane yields approached one another at high pressures and short exposure times was consistent with a step in which disilane decomposed to silane and silylene, followed by insertion of the silylene into a substrate molecule,

$$Si_2H_6 + h\nu \longrightarrow SiH_4 + SiH_2 \qquad [1]$$



$$SiH_2 + Si_2H_6 \xrightarrow{M} Si_3H_8 \qquad [2]$$

TABLE V - II

Effect of Substrate Pressure on the Product Yields from the 4 minute Photolysis of Si_2H_6 at Room Temperature

Pressure Si_2H_6 Torr	Products, μmoles				
	H_2	SiH_4	Si_3H_8	Si_4H_{10}	Σ
7	2.02	1.82	0.60	0.05	4.49
14	2.42	1.98	1.15	0.18	5.74
28	2.87	2.42	1.75	0.21	7.25
41	3.13	2.50	1.80	0.35	7.78
57	3.15	2.68	-	-	-
71	3.08	2.60	1.90	0.50	8.08
101	3.12	2.70	2.10	0.48	8.40
118	3.18	2.73	2.10	0.50	8.51
125	3.16	2.75	2.10	0.60	8.61
148	3.14	2.62	1.95	0.30	8.01
145[a]	3.03	2.72	2.20	0.45	8.40
400[b]	1.03	2.20	1.48	0.26	4.97

[a] 700 torr C_3H_8 added to Si_2H_6

[b] Si_2D_6, photolysis time 6 minutes.

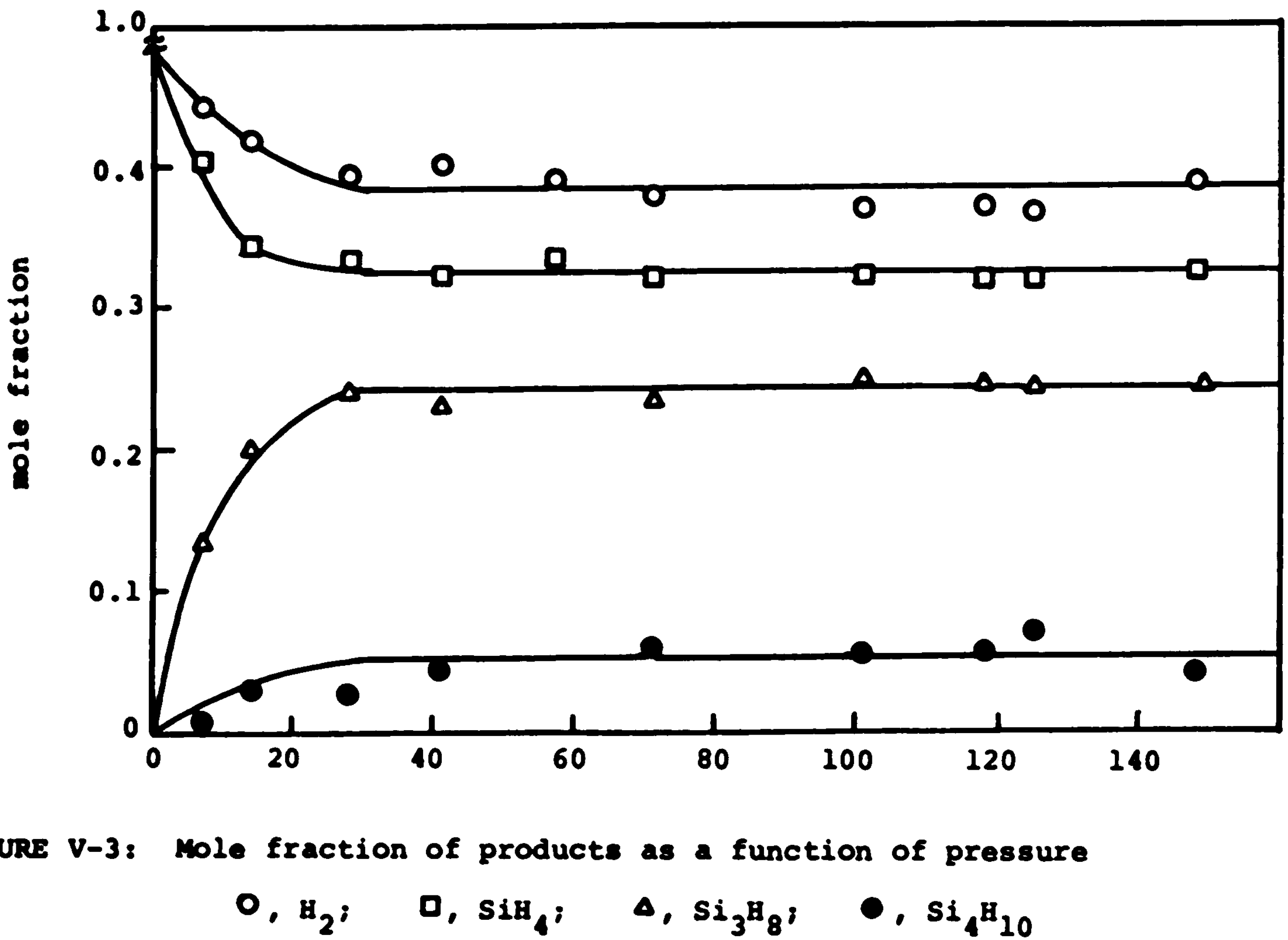


FIGURE V-3: Mole fraction of products as a function of pressure

○, H_2; □, SiH_4; △, Si_3H_8; ●, Si_4H_{10}

The same 1 to 1 correspondence was not observed for the other two products, hydrogen and tetrasilane. Hydrogen may be formed in any of three ways: 1) elimination of molecular hydrogen from the same silicon atom in disilane in a primary process, 2) elimination of molecular hydrogen from different atoms in disilane in a primary process, or 3) scission of a single silicon-hydrogen bond in the primary photolytic act followed by a metathetical hydrogen transfer from substrate to the hydrogen atom.

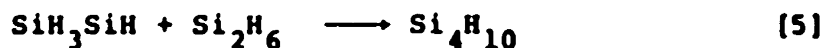
To examine these possibilities the deuterium labelling technique was employed. An equimolar mixture of Si_2H_6 and Si_2D_6 was photolyzed and the composition of the hydrogen fraction is shown in Table V-III. Clearly molecular elimination processes such as 1) and 2) were the major ones since the D_2 yield was greater than the HD yield. This would not be possible if all of the D_2 arose from deuterium atoms abstracting from Si_2D_6. Furthermore process 2),

$$Si_2H_6 + h\nu \longrightarrow H_2 + SiH_2SiH_2, \qquad [3]$$

would be the predominant mode of hydrogen formation since the diradical formed in 1),

$$Si_2H_6 + h\nu \longrightarrow H_2 + SiH_3SiH, \qquad [4]$$

would insert into a substrate molecule to give tetrasilane



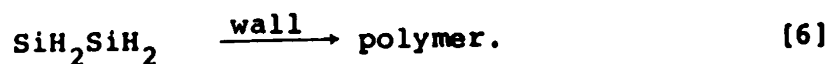
$$SiH_3SiH + Si_2H_6 \longrightarrow Si_4H_{10} \qquad [5]$$

TABLE V - III

Isotopic Composition of the Product Hydrogen

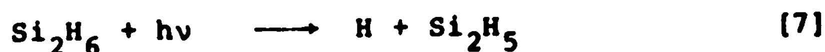
Pressure Torr		Percentage Composition		
Si_2H_6	Si_2D_6	H_2	HD	D_2
0	170	2.8	9.2	88.0
89.8	90.4	63.0	10.1	27.0
100	100	64.3	9.2	26.5

whereas the diradical formed in step [3], by analogy with the vuv-photolysis of methylsilane, would contribute only to polymer formation (61),



$$SiH_2SiH_2 \xrightarrow{wall} \text{polymer.} \qquad [6]$$

In order to delineate the radical processes in the system ethylene was added as a radical scavenger. The results are given in Table V-IV. Evidently monoradical reactions make only minor contributions to the product yields. The appearance of $Si_2H_5C_2H_5$ as a major product and the 50% reduction in the yield of tetrasilane was evidence for the disilanyl intermediate since the addition of Si_2H_5 to C_2H_4 is known to be a chain process in the presence of disilane, Chapter III. Coupled with the small yield of H atoms found in the isotopic studies this indicated some single silicon-hydrogen cleavage in a primary step



$$Si_2H_6 + h\nu \longrightarrow H + Si_2H_5 \qquad [7]$$

The 20 to 25% decrease in the SiH_4 and Si_3H_8 yields indicated that SiH_3 from a step such as

$$Si_2H_6 + h\nu \longrightarrow SiH_3 + SiH_3 \qquad [8]$$

could be contributing to the formation of these compounds in the unscavenged system. The slight decrease in the hydrogen yield was ascribed to an artifact of the system

in view of the fact that hydrogen atoms react with disilane five times faster than they add to ethylene, (Section 1c, Chapter III).

More evidence for SiH_3 intermediates was sought by adding NO as the radical scavenger; it has been shown to be an excellent agent for sorting out radical processes in the vacuum-ultraviolet photolyses of methyl silanes (60,61). The results are given in Table V-V. Obviously nitric oxide was not acting solely as a radical scavenger, since the monosilane and trisilane yields were definitely not decreased. The appearance of N_2 and N_2O together with the enhanced yield of H_2 was similar to the behaviour of NO in the mercury photosensitization system in Chapter III but the constitution of the condensable products was significantly different from that which had been observed in the photosensitization system (cf. Table III-VI). A check on the emission spectrum of the photolytic source showed that significant intensities were being emitted at wavelengths corresponding to absorption maxima in the spectrum of NO, Table V-VI. The electronically excited NO-sensitized decomposition of Si_2H_6 was not the purpose of this study so the "scavenging" by nitric oxide was not further pursued.

Another interesting result of the "NO scavenging", was the identification of the trace product i-Si_4H_{10} in the combined g.l.c.-mass spectrometric

TABLE V - IV

Four Minute Photolysis of 33 torr Si_2H_6 at Room Temperature in the Presence of Ethylene

Pressure C_2H_4 Torr	µmoles Product				
	H_2	SiH_4	Si_3H_8	Si_4H_{10}	$C_2H_5Si_2H_5$
0	2.80	2.40	1.60	0.31	-
1.5	2.62	2.40	-	0.19	0.94
3.9	2.67	1.98	1.26	0.17	1.78
8.7	2.60	1.81	1.27	0.16	1.80
13.3	2.65	2.14	1.22	0.19	1.80

TABLE V - V

Effect of NO on the Product Yields from the Photolysis of 100 torr of Si_2H_6 at Room Temperature

Photolysis Time	Pressure NO	Products, µmoles						
Minutes	Torr	N_2O	N_2	H_2	SiH_4	Si_3H_8	Si_4H_{10}	Total Condensables (-126°C)
3	0	-	-	1.23	0.98	-	-	1.54
3	4.00	1.70	2.28	2.19	0.90	-	-	2.36
3	4.54	1.75	2.44	2.59	1.05	-	-	3.08
3	0	-	-	1.66	1.35	1.18	0.17	1.35[a]
3	4.52	2.04	2.80	2.34	1.21	-	-	-
3	9.05	2.69	3.68	2.13	1.49	1.46	<0.05	4.00
14	0	-	-	4.39	3.78	3.14	0.33	3.47
14	5.52	11.0	15.2	6.80	7.09	4.45	0.19	13.1[b]

a Relative g.l.c. peak areas, $n\text{-}Si_4H_{10}:i\text{-}Si_4H_{10} = 100:3.1$

b Relative g.l.c. peak areas, $Si_3H_8:SiH_3OSiH_3:n\text{-}Si_4H_{10}:SiH_3OSi_2H_5:Si_5H_{10}O_5:i\text{-}Si_4H_{10}$ $= 100:40.7:5.7:3.1:1.2:0.15$.

TABLE V - VI

Emission Lines from Photolysis Lamp and Extinction Coefficients for NO and Si_2H_6

Emission Lines[a] nm	Relative Intensity	NO Absorption Maxima nm	ϵ_{NO} (decadic) $cm^{-1}atm^{-1}$	$\epsilon_{Si_2H_6}$ (decadic) $cm^{-1}atm^{-1}$
231.8 227.2 224.6	0.58 0.34 0.34	226.3	3.0	0
		215.1	4.3	0
		205.1	3.0	0.36
200.2 196.7 194.2	0.81 1.00 0.58	196.0	3.0	3.2

[a] Determined on a 0.5 m focal length Jarrell Ash Type 78-650 Seya Namioka vacuum scanning spectrograph.

analysis. The concentration of this product was below the detection limit of the g.l.c. unit employed for routine analyses. This product could be formed in either of two ways: 1) insertion of the silylsilylene radical into the Si-Si bond of the substrate, or 2) preferential insertion of silylene into a secondary silicon-hydrogen bond of the product trisilane. If 2) is the source of of the branched isomer the yield will be time dependent. A meaningful time study in which iso-tetrasilane can be monitored awaits a more sensitive analytical system or a monochromatic light source for photolysis of disilane which will not at the same time cause serious secondary photolysis of tetrasilane.

DISCUSSION

The foregoing data indicate that photolytic decomposition of disilane is a multi-step process,

$$Si_2H_6 + h\nu \longrightarrow SiH_4 + SiH_2 \quad [1]$$

$$\longrightarrow H_2 + SiH_2SiH_2 \quad [3]$$

$$\longrightarrow H_2 + SiH_3SiH \quad [4]$$

$$\longrightarrow H + Si_2H_5 \quad [7]$$

$$\longrightarrow SiH_3 + SiH_3. \quad [8]$$

For Si_2H_6 the hydrogen forming steps were found to be greater than those forming monosilane whereas the reverse was true for Si_2D_6. Thus the relative rates of the various steps is a function of the substituents on the silicon atoms though the absorption is largely associated with the silicon-silicon bond (2c). The tail of the absorption spectrum contains fine structure which is probably due to vibrational levels in the upper state. This indicates that the upper state is not totally repulsive in character. A total pressure of 850 torr did not reduce the total yield of products; so the lifetime of the excited state is of the order of the period of a few hundred vibrations. Since the absorbed photons carry energy of $\sim$140 kcal/einstein and there are five postulated primary steps, energy randomization must be efficient. This amount of energy is much greater than the endothermicities for decomposition into ground electronic state reaction products (Table V-VII), thus the fragments have excess energy to be dissipated. In step [1], for example, there is a maximum of 97 kcal/mole to be distributed among the vibrational, rotational, and translational modes of the two fragments. If each product receives its share of the total excess energy the SiH_2 will get 9/24 x 97 = 36 kcal/mole and the SiH_4, 61 kcal/mole. Equilibration of the translational and rotational modes with the Si_2H_6 bath will be efficient (153) leaving $\sim$12 kcal/mole

TABLE V - VII

Estimated Endothermicities of the Postulated Primary Reactions

Reaction		ΔH, kcal/mole
Si_2H_6	$\rightarrow SiH_4 + SiH_2$	43
	$\rightarrow H_2 + SiH_2SiH_2$	54
	$\rightarrow H_2 + SiH_3SiH$	41
	$\rightarrow H + Si_2H_5$	90
	$\rightarrow SiH_3 + SiH_3$	83

vibrational energy in SiH_2 and 37 kcal/mole in the SiH_4. The excess vibrational energy in the monosilane is well below the decomposition threshold of 56 kcal/mole (36) so vibrational relaxation will be its fate. The SiH_2 however, carrying up to 12 kcal/mole excess energy will insert into a substrate molecule, step [2], to form a chemically activated trisilane molecule.

It was observed that ca. 30 torr of substrate was required to stabilize the excited Si_3H_8 and Si_4H_{10} in the pressure study. If we assume a collision efficiency of $\sim$0.1 for stabilization of the excited molecule by Si_2H_6, a value can be calculated for the excess energy in the trisilane from the classical RRK expression and and the collision frequency.

The collision frequency is given by,

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi kT}{\mu}} \quad [A] \; sec^{-1}.$$

With an assumed collision diameter σ_{AB} of 4.5Å for the colliding pair and a pressure of 30 torr Si_2H_6, the collision frequency is

$$Z = 2.5 \times 10^8 \; sec^{-1}.$$

Multiplying this by the collision efficiency and setting it equal to the RRK expression for the trisilane molecule (Section 2b, Chapter III) we get,

$$k_{decomp} = 2.5 \times 10^{7} = 5.8 \times 10^{14}\left(\frac{E_{tot} - 45}{E_{tot}}\right)^{12.5} \text{ sec}^{-1}$$

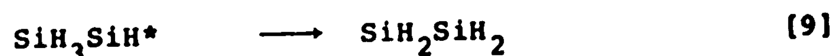
This equation is solved for E_{tot}, the total energy in the excited trisilane molecule, and gives,

$$E_{tot} = 60.6 \text{ kcal/mole.}$$

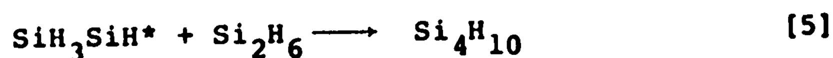
The exothermicity of step [2] is 44 kcal/mole, therefore the SiH_2 which inserted contained 16.6 kcal/mole excess energy. The agreement between this value and that calculated for the SiH_2 formed in the primary step indicates that the photonic energy is randomly distributed among the various available modes in the ground electronic state of the primary fragments.

Consider now the molecular hydrogen forming steps. It was found in the vacuum ultra-violet photolysis of ethane that the loss of a molecule of hydrogen from one carbon atom was the major mode of decomposition at 147 nm (154). The resultant "hot" ethylidene then rearranged to an excited molecule of ethylene which could be pressure stabilized. The product hydrogen from the photolysis of disilane is generated in a molecular process but if it were largely from one silicon atom one would expect the unscavengable tetrasilane yield from reaction [5] to approach the total hydrogen yield. The fact that it does not and that the fractional yield of tetrasilane remains

invariant over a 3-fold change in substrate concentration and a 25-fold increase in total pressure militates against a competition between a unimolecular isomerization step and a bimolecular insertion reaction for the removal of the silylene,



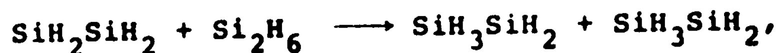
$$SiH_3SiH^* \longrightarrow SiH_2SiH_2 \qquad [9]$$



$$SiH_3SiH^* + Si_2H_6 \longrightarrow Si_4H_{10} \qquad [5]$$

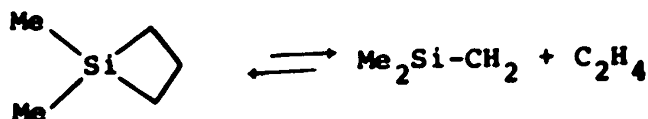
Therefore the molecular hydrogen arises mainly from a 1,2 elimination.

It was stated in the previous section that the 1,2 silicon diradical formed from this elimination was responsible for the observed polymer. This is contingent upon the 1,2 diradical being inert with respect to reaction with any other species in the system. This is not unexpected in the pure disilane system where reaction with the substrate is estimated to be quite endothermic,

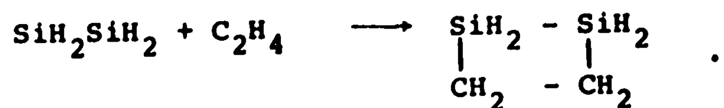


$$SiH_2SiH_2 + Si_2H_6 \longrightarrow SiH_3SiH_2 + SiH_3SiH_2,$$

$\Delta H \approx 21$ kcal/mole, and interaction with other radicals in the system could not compete with their removal by the substrate. The observation by Flowers and Gusel'nikov (155) that olefins inhibited the thermal decomposition of 1,1 dimethyl-1-silacylcobutane

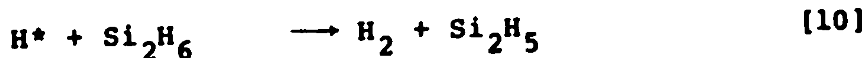


suggested that a simple 1:1 adduct might be formed between SiH_2SiH_2 and ethylene

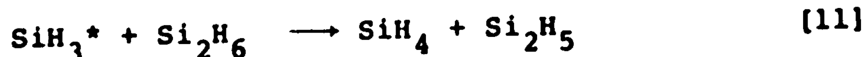


No volatile product was observed on the addition of ethylene, which might be ascribed to the addition. A minor product, less than 5% of the ethyldisilane, whose mass spectrum indicated a molecular weight corresponding to $C_4Si_2H_{14}$ was found at the highest concentration of ethylene. This could correspond to $(C_2H_5SiH_2)_2$, the product of the addition of two molecules of ethylene to the 1,2 diradical . This would indicate that this radical probably has some singlet character rather than existing strictly as two doublets, otherwise scavenging of the 1,2 diradical would be complete at much lower ethylene concentrations and the resultant absence of attenuating polymer would cause an increase in the hydrogen yield. It was concluded, therefore, that SiH_2SiH_2 was the polymer building unit, and SiH_3SiH was the precursor to the unscavengable n-tetrasilane.

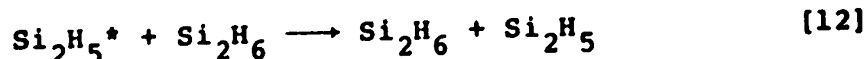
The monoradicals formed in the single bond homolysis steps, [7] and [8], have more than enough internal energy to overcome any energy barriers for metathesis with the substrate,



$$H^* + Si_2H_6 \longrightarrow H_2 + Si_2H_5 \qquad [10]$$

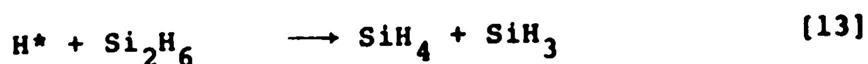


$$SiH_3^* + Si_2H_6 \longrightarrow SiH_4 + Si_2H_5 \qquad [11]$$



$$Si_2H_5^* + Si_2H_6 \longrightarrow Si_2H_6 + Si_2H_5 \qquad [12]$$

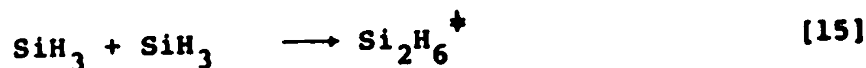
Additional reactions which the non-equilibrated radicals may undergo are,



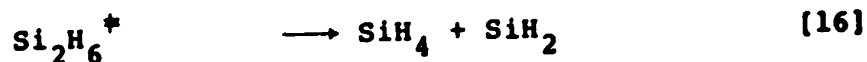
$$H^* + Si_2H_6 \longrightarrow SiH_4 + SiH_3 \qquad [13]$$

$$Si_2H_5^* + Si_2H_6 \longrightarrow Si_3H_8 + SiH_3 \qquad [14]$$

steps analogous to those for the mercury photosensitization of disilane. The thermally equilibrated radicals which result from these reactions undergo the usual disproportionations and combinations

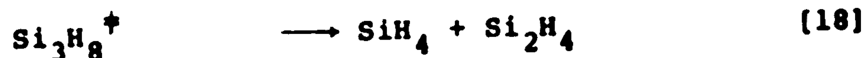


$$SiH_3 + SiH_3 \longrightarrow Si_2H_6^{\ddagger} \qquad [15]$$

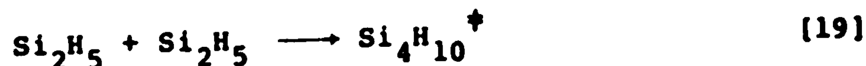


$$Si_2H_6^{\ddagger} \longrightarrow SiH_4 + SiH_2 \qquad [16]$$

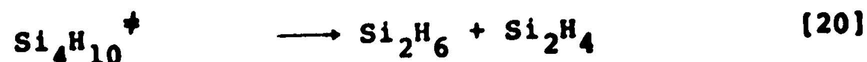
$$SiH_3 + Si_2H_5 \longrightarrow Si_3H_8^{\ddagger} \qquad [17]$$



$$Si_3H_8^{\ddagger} \longrightarrow SiH_4 + Si_2H_4 \qquad [18]$$



$$Si_2H_5 + Si_2H_5 \longrightarrow Si_4H_{10}^{\ddagger} \qquad [19]$$



$$Si_4H_{10}^{\ddagger} \longrightarrow Si_2H_6 + Si_2H_4 \qquad [20]$$

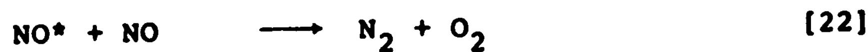
$$\xrightarrow{M} Si_4H_{10} \qquad [21]$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \qquad [2]$$

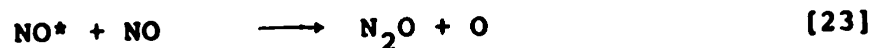
where the combination products $Si_2H_6^{\ddagger}$ and $Si_3H_8^{\ddagger}$ are unstable with respect to their decomposition products at

the pressures employed in this study (Section 2b, Chapter III).

The failure of NO to decrease the yield of any product except tetrasilane seems to indicate the transfer of electronic energy from an excited NO molecule to the disilane substrate which then decomposes to a molecule and a silylene, most probably SiH_4 and SiH_2. Electronically excited nitric oxide in its lowest doublet state is known to react with ground state NO to form oxygen atoms or molecules (142),



$$NO^* + NO \longrightarrow N_2 + O_2 \qquad [22]$$



$$NO^* + NO \longrightarrow N_2O + O \qquad [23]$$

It is the oxygen species which are most probably responsible for the large yield of disiloxane, SiH_3OSiH_3 which was observed in the condensables when NO was added. If this is so it means that the chemical cross-section for reaction between an excited NO molecule and a ground state NO is at least an order of magnitude larger than that for the reaction between NO* and Si_2H_6.

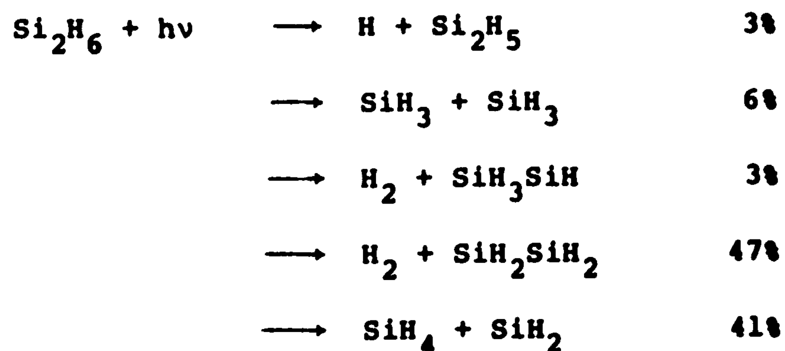
When the scavenging effect of NO on the tetrasilane yield is combined with the ethylene and isotopic mixture studied it is possible to estimate the contribution of the single bond scissions to the mechanism. Assuming that

1) $\Sigma\ Si_2H_5 = 2 \times$ (scavengable Si_4H_{10}) + (scavengable Si_3H_8)

2) $\Sigma\ SiH_3 \approx$ (scavengable SiH_4) + (scavengable Si_3H_8)

3) $SiH_4 + H_2$ = total primary processes

and utilizing the mole fractions extrapolated to zero time, the result is



$$Si_2H_6 + h\nu \longrightarrow H + Si_2H_5 \qquad 3\%$$

$$\longrightarrow SiH_3 + SiH_3 \qquad 6\%$$

$$\longrightarrow H_2 + SiH_3SiH \qquad 3\%$$

$$\longrightarrow H_2 + SiH_2SiH_2 \qquad 47\%$$

$$\longrightarrow SiH_4 + SiH_2 \qquad 41\%$$

The values estimated for the molecular processes represent upper limits since a minimum of 7% of the total hydrogen yield was HD in the isotopic mixture. This estimation does serve to contrast the direct photolysis with the mercury sensitization where the only primary step necessary to explain the products was a simple Si-H bond cleavage.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The present investigation has furthered knowledge of the production and reactions of silyl radicals derived from energy transfer between $Hg(6^3P_1)$ and ϕ-SiH_3, ϕ-SiD_3, Si_2H_6 and Si_2D_6; the metathetical reactions between H atoms and these compounds; and the reaction $CH_3 + Si_2D_6$. All of these systems were studied as a function of temperature. The results were compared with those from the direct photolysis of Si_2H_6 and Si_2D_6.

The result of transfer of energy from excited mercury atoms to ϕ-SiH_3 differs from that in the case of the analogous hydrocarbon, in that unit or near unit decomposition is realized. The decomposition occurs mainly at the Si-H bond and is a further example of the high reactivity of the hydric, polarizable, silicon hydride linkage toward the electrophilic $^3P_1$ mercury atoms. The observation that carbon-silicon bond cleavage and elimination of SiH_2 also contribute to the decomposition processes is ascribed to the interaction between the vacant d-orbitals of the silicon-atom and the π-cloud of the aromatic ring. Presumably the energy transferred from the excited mercury atom to the aromatic ring undergoes intramolecular partitioning before intermolecular

processes dissipate the energy of excitation.

The reaction between the excited mercury atoms and disilane was analogous to that between mercury and ethane in that hydrogen bond cleavage was the primary step. There was no evidence for Si-Si bond scission.

Reactions of silyl radicals are similar to those of alkyl radicals, with important differences which reflect on the properties of silicon. Monosilyl radicals do not recombine at pressures up to one atmosphere. Similarly no combination products from methyl plus disilanyl or monosilyl plus disilanyl were observed at total pressures up to one atmosphere. Tetrasilane, the combination product of two disilanyl radicals was observed, however. This indicated that as the degree of complexity of the newly formed molecule increased, i.e. as the total number of ways of partitioning the energy of the newly formed bond became greater, the lifetime of the species increased and collisional stabilization was possible. These observations reflect the fact that silanes have available to them a low energy decomposition path which leads to a stable silane molecule and a silylene.

Disproportionations of silyl radicals are not readily observed since stable multiple bonded silicon compounds are unknown. The simplest disproportionation product SiH_2 has a singlet ground state and inserts into substrate to give a disilane. The head-to-tail

disproportionation product of two disilanyl radicals, SiH_2SiH_2, is the most probable precursor to the solid polymer observed on the cell walls and the presence of this polymer suggests that the reaction does occur. Disproportionation to combination ratios can be determined only by difference because of this reaction.

Another difference between alkane and silane reactions is the accessability of pentavalent silicon atoms. This makes possible the displacement reaction observed in reactions between hydrogen atoms and disilane at room temperature and the displacement reactions between disilanyl radicals and disilane and phenylsilyl radicals and phenylsilane at somewhat higher temperatures. It was found that these displacement reactions could compete with the "conventional" metathesis reactions.

Monosilyl and disilanyl radicals were found to be stable with respect to unimolecular decomposition at temperatures up to 220°C. This was attributed to the inability of silicon to participate in multiple bonding in the case of disilanyl.

Direct photolysis of disilane was similar to that of ethane and methylsilane in that molecular processes were the main mode of decomposition. Homolysis of single bonds, both Si-Si and Si-H contributed less than 10 per cent to the overall process. Significantly the proportion

of substrate which decomposed by a given path was a function of the substituents on the silicon atom. Deuterium substitution favoured processes in which loss occurred from one silicon atom moreso than did protium substitution. This was not observed for methyl silane or ethane.

The surface of the field of silyl radical reactions has only been scratched. The greatest present need is still more reliable thermodynamic values for silicon and organosilicon compounds and temperature studies of photolysis systems offers one possibility of extending our present knowledge in this field. Studies along this line should also lead to a greater understanding of the mechanisms of energy transfer and inter- and intramolecular partitioning of energy.

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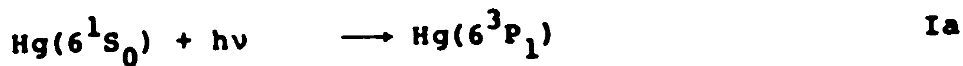
APPENDIX A

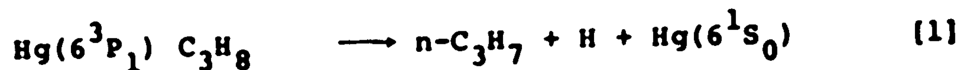
Propane Actinometry

"The quantum yield of hydrogen production is 0.46 at room temperature and 14 cm pressure, rising to 0.50 at high pressures. Hydrogen production is a linear function of time." (122) This observation made propane a convenient actinometer for $Hg(6^3P_1)$ photosensitization reactions. At that time it was felt that the quantum yield deficit was due to "physical quenching" of the electronically excited mercury atom by the propane molecules. Back (123) found that the rate of hydrogen production was not a linear function of time in the initial stages of the reaction, instead it decreased with time to a limiting value. This is characteristic of a build-up of a secondary product to a concentration such that it can compete successfully for the products of the primary step. Such a product is the olefin formed by the disproportionation of the alkyl free radicals formed in the primary step.

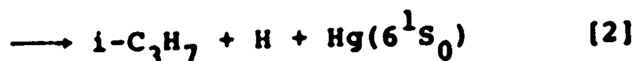
The reaction scheme proposed by Back included



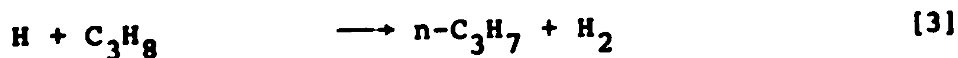
$$Hg(6^1S_0) + h\nu \longrightarrow Hg(6^3P_1) \qquad \text{Ia}$$



$$Hg(6^3P_1)\ C_3H_8 \longrightarrow n\text{-}C_3H_7 + H + Hg(6^1S_0) \qquad [1]$$



$$\longrightarrow i\text{-}C_3H_7 + H + Hg(6^1S_0) \qquad [2]$$


$$H + C_3H_8 \longrightarrow n\text{-}C_3H_7 + H_2 \qquad [3]$$

$$\longrightarrow i\text{-}C_3H_7 + H_2 \qquad [4]$$

$$n\text{-}C_3H_7 + n\text{-}C_3H_7 \longrightarrow C_6H_{14} \qquad [5]$$

$$\longrightarrow C_3H_6 + C_3H_8 \qquad [6]$$

$$i\text{-}C_3H_7 + n\text{-}C_3H_7 \longrightarrow C_6H_{14} \qquad [7]$$

$$\longrightarrow C_3H_6 + C_3H_8 \qquad [8]$$

$$i\text{-}C_3H_7 + i\text{-}C_3H_7 \longrightarrow C_6H_{14} \qquad [9]$$

$$\longrightarrow C_3H_6 + C_3H_8 \qquad [10]$$

$$H + C_3H_6 \longrightarrow i\text{-}C_3H_7 \qquad [11]$$

Steady state treatment of this scheme yields[a]

$$\frac{d[n]}{dt} = 0 = k_1[Hg^*][S] + k_3[H][S] - 2(k_5+k_6)[n]^2 - (k_7+k_8)[n][i] \qquad [12]$$

$$\frac{d[i]}{dt} = 0 = k_2[Hg^*][S] + k_4[H][S] + k_{11}[H] - (k_7+k_8)[n][i] - 2(k_9+k_{10})[i]^2 \qquad [13]$$

$$\frac{d[H]}{dt} = 0 = (k_1+k_2)[Hg^*][S] - (k_3+k_4)[H][S] - k_{11}[H] \qquad [14]$$

The rate constants for radical-radical reactions can be associated with the collision frequency which is proportional to the product of the collision diameter and the square root of the reciprocal of the reduced mass

---

[a] S = substrate, C_3H_8 Ol = olefin, C_3H_6
n = $n\text{-}C_3H_7$ i = $i\text{-}C_3H_7$

of the colliding species. For the propyl radicals in this system the following relation will hold

$$2K = 2(k_5+k_6) = (k_7+k_8) = 2(k_9+k_{10}) \qquad [16]$$

and from this

$$[n] - [i] = \left(\frac{\phi I_a}{K}\right)^{1/2} \qquad [17]$$

Knowing that $k_1/k_2 = 0.101$ and $k_3/k_4 = 0.0417$ from the work of Campbell et al. (124,125), substitution of [17] into [12] and [13] gives

$$0 = 0.0917\ I_a + \frac{\phi I_a k_3(S)}{(k_3+k_4)[S]+k_{11}(01)} - 2K(n)^2$$

$$- 2K(n)((\phi I_a/K)^{1/2} - (n)) \qquad [18]$$

$$= 0.0917\ \phi I_a + \frac{0.0417k_4(S)\ \phi I_a}{1.0417k_4(S)+k_{11}(01)} - 2(\ I_a)^{1/2}(n)-K^{1/2}$$

$$(n) = \tfrac{1}{2}(\phi I_a/K)^{1/2}\ \frac{(0.1372k_4(S)+0.0917k_{11}(01))}{(1.0417k_4(S)+k_{11}(01))}$$

$$(i) = \tfrac{1}{2}(\phi I_a/K)^{1/2}\ \frac{(1.946k_4(S)+1.9083k_{11}(01))}{(1.0417k_4(S)+k_{11}(01))} \qquad [19]$$

The condition of a photostationary concentration of propylene imposes the restriction

$$\frac{d(C_3H_6)}{dt} = 0 = k_6(n) + k_8(n)(i) + k_{10}(i)^2 - k_{11}(H)(01) \qquad [20]$$

and the relation between the rate of abstraction from propane by hydrogen atoms and the rate of addition to propylene is given by

$$\frac{R(abs)}{R(add)} = \frac{\phi I_a}{(k_6(n)+k_8(n)(i)+k_{10}(i)} - 1 \qquad [21]$$

Starting from the approximation that $(k_3+k_4)(S) = k_{10}(01)$ in equations [18] and [19] it is found from substitution in [21] that (R(abs)/R(add)) reduces to 1.40 when the disproportionation to combination ratios from Terry and Futrell (126) are inserted.

This predicts a value of 0.58 for the quantum yield of hydrogen from the mercury photosensitization of high pressures of propane when the rate of hydrogen production is constant. This can be compared to the experimental value of 0.581 ± 0.012 obtained when nitrous oxide with 1% 1-butene added to scavenge the oxygen atoms was used as the actinometer, (Table A-I).

TABLE A - I

Rate of Formation of Non-condensables in the Determination of Absorbed Light Intensities

	1000 torr C_3H_8	500 torr N_2O + 4.0 torr 1-C_4H_8
Time min	$\frac{d[H_2]}{dt}$ μmoles/min	$\frac{d[N_2]}{dt}$ μmoles/min
10	0.131	
14	0.137	
12	0.138	
10	0.137	
11.5	0.137	
10		0.241
11		0.244
6		0.235
10		0.232
10		0.236
10		0.236
8		0.244

If $\Phi(H_2)$ = 0.50; I_a = 0.274 μEinsteins/min

If $\Phi(N_2)$ = 1.00; I_a = 0.236 ± 0.004 Einsteins/min

In terms of nitrous oxide actinometry then $\Phi(H_2)$ from propane is

$$\Phi(H_2) = 0.58 \pm 0.012 \text{ Moles/Einstein.}$$

APPENDIX B: MASS SPECTRA OF PRODUCTS

The relative intensities of the m/e ratios in the mass spectra were determined at an ionization voltage of ca 70 volts. The symbol "p" indicates the parent compound.

TABLE B - I

A from Si_2H_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	9	Si^+
29	5	SiH^+
30		
31	6	SiH_3^+
45		
72	17	Si_2O^+
73	34	Si_2HO^+
74	12	$Si_2H_2O^+$
75	100	$Si_2H_3O^+$
76	54	$Si_2H_4O^+$
77	65	$Si_2H_5O^+$
78	8	$Si_2H_6O^+$
106	6	$Si_3H_6O^+$
107	15	$Si_3H_7O^+$
p108	15	$Si_3H_8O^+$

A from Si_2D_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	11	Si^+
30	8	SiD^+
32		
34	9	SiD^+
46	5	$SiDO^+$
72	14	Si_2O^+
74	27	Si_2DO^+
76	8	$Si_2D_2O^+$
78	100	$Si_2D_3O^+$
80	40	$Si_2D_4O^+$
82	48	$Si_2D_5O^+$
112	(4)	$Si_3D_6O^+$
114	9	$Si_3D_7O^+$
p116	11	$Si_3D_8O^+$

TABLE B - II

Si_3H_8 from Si_2H_6 + Hg*

m/e	R.I.	Postulated Ion
28	4	Si^+
29	3	SiH^+
30		SiH_2^+
31		SiH_3^+
56		
57		
58	31	$Si_2H_2^+$
59	10	$Si_2H_3^+$
60	100	$Si_2H_4^+$
61	18	$Si_2H_5^+$
62	9	$Si_2H_6^+$
84	10	Si_3^+
85	13	Si_3H^+
90	12	$Si_3H_6^+$
p92	11	$Si_3H_8^+$

Si_3D_8 from Si_2D_6 + Hg*

m/e	R.I.	Postulated Ion
28	2	Si^+
30	5	SiD^+
32		SiD_2^+
34	5	SiD_3^+
56	8	Si_2^+
58	18	Si_2D^+
60	44	$Si_2D_2^+$
62	13	$Si_2D_3^+$
64	100	$Si_2D_4^+$
66	17	$Si_2D_5^+$
68		
84	10	Si_3^+
86	12	Si_3D^+
96	9	$Si_3D_6^+$
98	6	$Si_3D_7^+$
p100	8	$Si_3D_8^+$

TABLE B - III

Si_4H_{10} from Si_2H_6 + Hg*

m/e	R.I.	Postulated Ion
28	26	Si^+
29	13	SiH^+
30	19	SiH_2^+
31	19	SiH_3^+
56	11	Si_2^+
57	19	Si_2H^+
58	59	$Si_2H_2^+$
59	20	$Si_2H_3^+$
60	29	$Si_2H_4^+$
61		
62		
84	27	Si_3^+
85	38	Si_3H^+
86	19	$Si_3H_2^+$
87	16	$Si_3H_3^+$
88	38	$Si_3H_4^+$
89	19	$Si_3H_5^+$
90	100	$Si_3H_6^+$
91	27	$Si_3H_7^+$

Si_4D_{10} from Si_2D_6 + Hg*

m/e	R.I.	Postulated Ion
28	61	Si^+
30	25	SiD^+
32	35	SiD_2^+
34	33	SiD_3^+
56	16	Si_2^+
60	86	$Si_2D_2^+$
62	27	$Si_2D_3^+$
64	44	$Si_2D_4^+$
66	12	$Si_2D_5^+$
68	16	$Si_2D_6^+$
84	26	Si_3^+
86	37	Si_2D^+
88	13	$Si_3D_2^+$
90	10	$Si_3D_3^+$
92	34	$Si_3D_4^+$
94	15	$Si_3D_5^+$
96	100	$Si_3D_6^+$
98	23	$Si_3D_7^+$
100		

TABLE B - III (cont'd)

Si_4H_{10} from Si_2H_6 + Hg*			Si_4D_{10} from Si_2D_6 + Hg*		
m/e	R.I.	Postulated Ion	m/e	R.I.	Postulated Ion
92	13	$Si_3H_8^+$	112	9	Si_4^+
112	17	Si_4^+	114	8	Si_4D^+
113	15	Si_4H^+	p132	3	Si_4D_{10}
p122	5	$Si_4H_{10}^+$			

TABLE B - IV

E from Si_2H_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	34*	Si^+
29	10	
30		
31	10	SiH_3^+
45	5	$SiHO^+$
47	7	SiH_3O^+
60	8	SiO_2^+
72	12	Si_2O^+
73	28	Si_2HO^+
74	11	$Si_2H_2O^+$
75	57	$Si_2H_3O^+$
76	16	$(Si_2H_4O^+)$
77	58	$(Si_2H_5O^+)$
78	6	$(Si_2H_6O^+)$
89	7	$Si_2HO_2^+$
91	33	$Si_2H_3O_2^+$
118	5	$Si_3H_2O_2^+$
119	11	$Si_3H_3O_2^+$
120	14	$Si_3H_4O_2^+$

E from Si_2D_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	16	Si^+
30		
32		
34	6	SiD_3^+
46	8	$SiDO^+$
50	(4)	SiD_3O^+
62	6	$SiDO_2^+$
72	8	Si_2O^+
74	18	Si_2DO^+
76	6	$Si_2D_2O^+$
78	29	$Si_2D_3O^+$
90	7	$Si_2DO_2^+$
94	40	$Si_2D_3O_2^+$
120	(3)	$Si_3D_2O_2^+$
122	7	$Si_2D_3O_2^+$
124	10	$Si_2D_4O_2^+$

TABLE B - IV (cont'd)

E from Si_2H_6 + NO + Hg*			E from Si_2D_6 + NO + Hg*		
m/e	R.I.	Postulated Ion	m/e	R.I.	Postulated Ion
121	26	$Si_3H_5O_2^+$	126	31	$Si_3D_5O_4^+$
122	14	$Si_3H_6O_2^+$	128	11	$Si_3D_6O_2^+$
123	100	$Si_3H_7O_2^+$	130	100	$Si_3D_7O_2^+$
124	13	$Si_3H_8O_2^+$	132	10	$Si_3D_8O_2^+$
125	8	?			
137	21	$Si_3H_5O_3^+$	142	11	$Si_3D_5O_3^+$

TABLE B - V

B from Si_2H_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	12	Si^+
29		
30	7	SiH_2^+
31		
73	(4)	Si_2HO^+
75	17	$Si_2H_3O^+$
77	10	$Si_2H_5O^+$
91	8	$Si_2H_3O_2^+$
121	6	$Si_3H_5O_2^+$
123	10	$Si_3H_7O_2^+$
135	12	$Si_3H_3O_3^+$
137	100	$Si_3H_5O_3^+$
138	14	$Si_3H_6O_3^+$
139	11	$Si_3H_7O_3^+$
169	8	$Si_4H_9O_3^+$
183	7	$Si_4H_7O_4^+$

B from Si_2D_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	10	Si^+
30		
32		
34	5	SiD_3^+
46	8	$SiDO^+$
74	7	Si_2DO^+
78	20	$Si_2D_3O^+$
82	10	$Si_2D_5O^+$
94	10	$Si_2D_3O_2^+$
126	5	$Si_3D_5O_2^+$
130	5	$Si_3D_7O_2^+$
138	11	$Si_3D_3O_3^+$
142	100	$Si_3D_5O_3^+$
144	10	$Si_3D_6O_3^+$
178	6	$Si_4D_9O_3^+$
190	(2)	$Si_4D_7O_4^+$

TABLE B - VI

C from Si_2H_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	14	Si^+
31	5	SiH_3^+
46		
47	7	SiH_3O^+
72	8	Si_2O^+
73	18	Si_2HO^+
74	9	$Si_2H_2O^+$
75	96	$Si_2H_3O^+$
76	15	$Si_2H_4O^+$
77	31	$Si_2H_5O^+$
89	5	$Si_2HO_2^+$
91	13	$Si_2H_3O_2^+$
118	7	$Si_3H_2O_2^+$
119	15	$Si_3H_3O_2^+$
120	20	$Si_3H_4O_2^+$
121	100	$Si_3H_5O_2^+$
122	26	$Si_3H_6O_2^+$
123	96	$Si_3H_7O_2^+$
124	(12)	$(Si_3H_8O_2^+)$

C from Si_2D_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	22	Si^+
30	8	SiD^+
34	12	SiD_3^+
46	8	$SiDO^+$
72	11	Si_2O^+
74	28	Si_2DO^+
76	9	$Si_2D_2O^+$
78	100	$Si_2D_3O^+$
80	8	$Si_2D_4O^+$
82	33	$Si_2D_5O^+$
90	5	$Si_2DO_2^+$
94	23	$Si_2D_3O_2^+$
120	6	$Si_3D_3O_2^+$
122	13	$Si_3D_3O_2^+$
124	15	$Si_3D_4O_2^+$
126	93	$Si_3D_5O_2^+$
128	23	$Si_3D_6O_2^+$
130	87	$Si_3D_7O_2^+$
132	8	$(Si_3D_8O_2)^+$

TABLE B - VI (cont'd)

	C from Si_2H_6 + NO + Hg*	
m/e	R.I.	Postulated Ion
137	14	$Si_3H_5O_3^+$
153	11	$Si_4H_9O_2^+$
167	(4)	$Si_4H_7O_3^+$
183	(3)	$Si_4H_7O_4^+$

	C from Si_2D_6 + NO + Hg*	
m/e	R.I.	Postulated Ion
142	5	$Si_3D_5O_3^+$
162	7	$Si_4D_9O_2^+$
174	(1)	$Si_4D_7O_3^+$
190	(1)	$Si_4D_7O_4^+$

TABLE B - VII

D from Si_2H_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	5	Si^+
30	4	SiH_2^+
72	8	Si_2O^+
73	17	Si_2HO^+
74	4	$Si_2H_2O^+$
75	100	$Si_2H_3O^+$
76	10	$Si_2H_4O^+$
77	9	$Si_2H_5O^+$
103	4	$Si_3H_3O^+$
105	22	$Si_3H_5O^+$
106	28	$Si_3H_6O^+$
107	22	$Si_3H_7O^+$
108	4	$(Si_3H_8O^+)$
135	5	$Si_4H_7O^+$
137	4	$Si_4H_9O^+$
p138	(1)	$Si_4H_{10}O^+$

D from Si_2D_6 + NO + Hg*

m/e	R.I.	Postulated Ion
28	8	Si^+
30	7	SiD^+
34	8	SiD_3^+
58	6	Si_2D^+
60	5	$Si_2D_2^+$
62	4	$Si_2D_3^+$
72	16	Si_2O^+
74	30	Si_2DO^+
76	6	$Si_2D_2O^+$
78	100	$Si_2D_3O^+$
80	9	$Si_2D_4O^+$
82	6	$Si_2D_5O^+$
110	23	$Si_3D_5O^+$
112	26	$Si_3D_6O^+$
114	22	$Si_3D_7O^+$
142	(2)	$Si_4D_7O^+$
146	(2)	$Si_4D_9O^+$

TABLE B - VIII

Monosilane Fraction from $Si_2H_6 + Si_2D_6 + Hg^*$[a]

m/e	R.I.	Postulated Ion
36	9	
35	19	
34	292	SiD_3^+
33	246	SiD_2H^+
32	725	SiD_2^+, SiH_2D^+
31	912	$SiDH^+$, SiH_3^+
30	1000	SiD^+, SiH_2^+
29	263	SiH^+
28	532	Si^+

a. Assumption of no isotope effect for cracking pattern gives

$SiD_4:SiD_3H:SiH_3D:SiH_4 = 25:37:42:54$

TABLE B - IX

Tetrasilane Fraction from $Si_2H_6 + Si_2D_6 + Hg^*$

m/e	R.I.	Postulated Ion	m/e	R.I.	Postulated Ion
28	72	Si^+	86	47	$Si_3H_2^+$, Si_3D^+
29	19	SiH^+	87	28	$Si_3H_3^+$, Si_3HD^+
30	29	SiH_2^+, SiD^+	88	46	$Si_3H_4^+$, $Si_3H_2D^+$, $Si_3D_2^+$
31	27	SiH_3^+, $SiHD^+$	89	45	
32	21	SiD_2^+	90	85	
56	23	Si_2^+	91	100	$Si_3H_5D^+$ (?)
57	30	Si_2H^+	92	65	
58	83	$Si_2H_2^+$, Si_2D^+	93	38	
59	57	$Si_2H_3^+$, Si_2HD^+	94	23	
60	54	$Si_2H_4^+$, $Si_2H_2D^+$, $Si_2D_2^+$	95	12	
61	36		112	30	
62	23		113	23	
63	13		114	16	
64	6		115	8	
77	7	$Si_2H_5O^+$	116	6	
84	53	Si_3^+	117	5	
85	59	Si_3H^+			

TABLE B - IX (cont'd)

Tetrasilane Fraction from Si_2H_6 + Si_2D_6 + Hg* (cont'd)

m/e	R.I.	Postulated Ion
118	6	
119	8	
120	8	
121	8	
122	8	
123	7	
124	5	
125	4	
126	2	
127	2	
128	1	$Si_4D_8^+$

TABLE B - X

Monosilane Fraction from $H_2 + Si_2D_6 + Hg^*$

m/e	R.I.[a]	R.I.[b]	R.I.[c]	Postulated Ion
36	20	25	20	
35	50	49	53	
34	694	681	710	SiD_3^+
33	679	652	576	SiD_2H^+
32	1000	1000	1000	SiD_2^+
31	562	523	438	$SiDH^+$
30	350	337	312	SiD^+
29	85	98	40	SiH^+
28	160	193	-	Si^+

a. H_2/Si_2D_6 = (500 torr)/(2 torr).

b. H_2/Si_2D_6 = (600 torr)/(6 torr).

c. $H_2/C_3D_8/Si_2D_6$ = (1200 torr)/(150 torr)/(15 torr).

TABLE B - XI

Mass Spectra of Disilane and the Deuterodisilanes and the Percentage Composition of the Disilane from $H_2 + SiH_4 + SiD_4 + Hg^*$

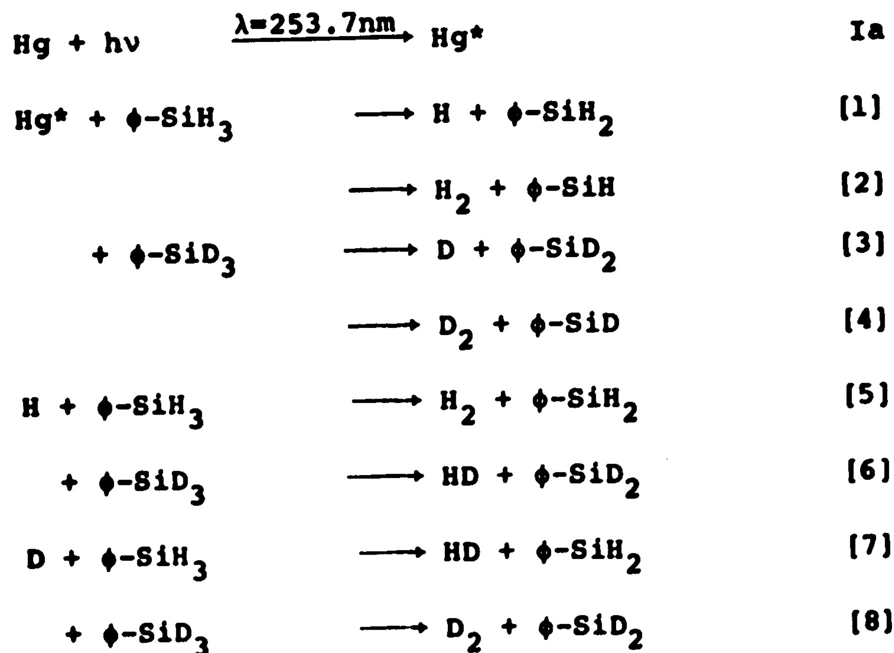
m/e	Si_2D_6	Si_2D_5H	Si_2D_4H	$Si_2D_3H_3$	$Si_2D_2H_4$	Si_2DH_5	Si_2H_6 [b]	Sample [b]
68	60.6	11.7	5.0	0	0	0	0	100
67	4.7	60.2	14.7	6.0	0	0	0	71
66	33.0	51.8	62.5	15.0	8.2	0	0	407
65	13.8	48.8	58.6	65.0	17.6	6.8	0	328
64	100	78.6	57.2	54.7	79.5	16.7	5.2	700
63	3.2	100	100	68.7	60.1	64.2	9.5	814
62	24.4	50.5	84.7	100	100	51.2	55.9	1228
61	11.2	29.3	41.4	49.0	83.1	100	44.4	957
60	79.6	88.0	68.8	66.7	58.3	69.5	100	1957
59	4.7	48.8	65.8	74.4	73.4	51.6	40.1	971
58	36.2	51.4	53.9	71.0	67.3	70.6	69.9	1485
57	3.4	13.8	20.4	25.6	33.0	32.2	35.6	700
56	23.2	36.1	36.4	40.0	35.9	28.1	24.6	814
% Composition	9.7	4.4	19.1	0.3	1.2	8.1	57.2	

[a] Reference 63 [b] This work.

APPENDIX C

Derivation of the Expression for the Fraction of Molecular Hydrogen Formation in the Mercury Photosensitization of Phenylsilane

The following reaction scheme is considered for the production of hydrogen in the $Hg(6^3P_1)$ sensitization of phenylsilane:



$$Hg + h\nu \xrightarrow{\lambda=253.7nm} Hg^* \qquad Ia$$

$$Hg^* + \phi\text{-}SiH_3 \longrightarrow H + \phi\text{-}SiH_2 \qquad [1]$$

$$\longrightarrow H_2 + \phi\text{-}SiH \qquad [2]$$

$$+ \phi\text{-}SiD_3 \longrightarrow D + \phi\text{-}SiD_2 \qquad [3]$$

$$\longrightarrow D_2 + \phi\text{-}SiD \qquad [4]$$

$$H + \phi\text{-}SiH_3 \longrightarrow H_2 + \phi\text{-}SiH_2 \qquad [5]$$

$$+ \phi\text{-}SiD_3 \longrightarrow HD + \phi\text{-}SiD_2 \qquad [6]$$

$$D + \phi\text{-}SiH_3 \longrightarrow HD + \phi\text{-}SiH_2 \qquad [7]$$

$$+ \phi\text{-}SiD_3 \longrightarrow D_2 + \phi\text{-}SiD_2 \qquad [8]$$

Applying steady-state approximations

$$R_{Hg^*} = I_a - [Hg^*]\{(k_1+k_2)[LI] + (k_3+k_4)[HE]\} = 0$$

$$R_H = k_1[Hg^*][LI] - [H]\{k_5[LI] + k_6[HE]\} = 0$$

$$R_D = k_3[Hg^*][HE] - [D]\{k_7[LI] + k_8[HE]\} = 0$$

and solving for the steady-state concentrations of the intermediates gives

$$[Hg^*] = \frac{I_a}{(k_1+k_2)[LI] + (k_3+k_4)[HE]}$$

$$[H] = \frac{k_1[Hg^*][LI]}{k_5[LI] + k_6[HE]}$$

$$[D] = \frac{k_3[Hg^*][HE]}{k_7[LI] + k_8[HE]}$$

The rates of formation of the hydrogen products are

$$R_{H_2} = k_2[Hg^*][LI] + k_5[H][LI]$$

$$R_{HD} = k_6[H][HE] + k_7[D][LI]$$

$$R_{D_2} = k_4[Hg^*][LI] + k_8[D][HE]$$

and the total rate of formation of hydrogen is

$$R_{(H_2+HD+D_2)} = k_2[Hg^*][LI] + (k_5[LI]+k_6[HE])[H] + (k_7[LI]+ k_8[HE])[D] + k_4[Hg^*][LI]$$

$$= (k_1+k_2)[Hg^*][LI] + (k_3+k_4)[Hg^*][HE].$$

The mole fraction of each of the isotopic hydrogen components then becomes

$$\frac{R_{H_2}}{R_{(H_2+HD+D_2)}} = X_{H_2} = \frac{k_2[LI]}{(k_1+k_2)[LI]+(k_3+k_4)[HE]}$$

$$+ \frac{k_5[LI]k_1[LI]}{(k_5[LI]+k_6[HE])((k_1+k_2)[LI]+(k_3+k_4)[HE])}$$

$$= \left(k_2 + \frac{k_1k_5[LI]}{k_5[LI]+k_6[HE]}\right)\left(\frac{[LI]}{(k_1+k_2)[LI]+(k_3+k_4)[HE]}\right) \quad \text{(i)}$$

$$\frac{R_{D_2}}{R_{(H_2+HD+D_2)}} = X_{D_2} = \left(k_4 + \frac{k_3k_8[HE]}{k_7[LI]+k_8[HE]}\right)\left(\frac{[HE]}{(k_1+k_2)[LI]+(k_3+k_4)[HE]}\right) \quad \text{(ii)}$$

$$\frac{R_{HD}}{R_{(H_2+HD+D_2)}} = X_{HD} = \left\{\frac{k_6[HE]\cdot k_1[LI]}{k_5[LI]+k_6[HE]} + \frac{k_7[LI]k_3[HE]}{k_7[LI]+k_8[HE]}\right\}$$

$$\left\{\frac{1}{(k_1+k_2)[LI]+(k_3+k_4)[HE]}\right\} . \quad \text{(iii)}$$

Also the mole fractions of the phenylsilane and phenylsilane-d_3 respectively are expressed as

$$X_{LI} = \frac{[LI]}{[LI] + [HE]} \quad \text{(iv)}$$

$$X_{HE} = \frac{[HE]}{[LI] + [HE]} \quad \text{(v)}$$

The expression for the ratio of the mole fraction of D_2 to the mole fraction of phenylsilane-d_3 then becomes on combining (ii) and (v)

$$\left(\frac{X_{D_2}}{X_{HE}}\right) = \left(k_4 + \frac{k_3 k_8 [HE]}{k_7 [LI] + k_8 [HE]}\right)\left(\frac{[LI] + [HE]}{(k_1+k_2)[LI] + (k_3+k_4)[HE]}\right)$$

which at the limit $[HE] \rightarrow 0$, reduces to

$$\frac{X_{D_2}}{X_{HE}} = \frac{k_4}{k_1 + k_2} \ .$$

Division of (iii) by (iv) gives,

$$\left(\frac{X_{HD}}{X_{LI}}\right) = \left\{\frac{k_1 k_6 [HE]}{k_5 [LI] + k_6 [HE]} + \frac{k_3 k_7 [HE]}{k_7 [LI] + k_8 [HE]}\right\}\left\{\frac{[LI] + [HE]}{(k_1+k_2)[LI] + (k_3+k_4)[HE]}\right\}$$

which as $[LI] \rightarrow 0$ reduces to

$$\left(\frac{X_{HD}}{X_{LI}}\right)_{[LI] \rightarrow 0} = \frac{k_1}{k_3 + k_4} + \left(\frac{k_7}{k_8}\right)\left(\frac{k_3}{k_3 + k_4}\right).$$

Similar treatment of equations (iii) and (v) gives

$$\left(\frac{X_{HD}}{X_{HE}}\right)_{[HE] \rightarrow 0} = \left(\frac{k_6}{k_5}\right) \cdot \frac{k_1}{k_1 + k_2} + \frac{k_3}{k_1 + k_2} \ .$$

<u>Correction for isotopic impurity in phenylsilane-$\underline{d}_3$.</u>

When $k_1 = k_3$ and $k_2 = k_4 = 0$

$$[Hg^*] = \frac{I_a}{k_1([LI] + [HE])} .$$

Taking into account the hydrogen content of the silyl side chain the new expressions for the steady-state approximations are,

$$R_D = 0 = k_3 Hg^*[HE](\chi) - k_7[D][LI] - k_8[D][HE](\chi) - k_7[D][HE](1-\chi)$$

$$R_H = 0 = k_1 Hg^*[LI] + k_3 Hg^*[HE](1-\chi) - k_5[H][LI] - k_5[H][HE](1-\chi) - k_6[H][HE](\chi),$$

from which the atom concentrations are,

$$D = \frac{k_3 Hg^*[HE](\chi)}{k_7\{[LI]+[HE](1-\chi)\} + k_8[HE](\chi)} = \frac{X_{HE}\ I_a(\chi)}{k_7\{[LI]+[HE](1-\chi)\}+k_8[HE](\chi)}$$

$$H = \frac{k_1 Hg^*[LI]+k_3 Hg^*[HE](1-\chi)}{k_5\{[LI]+[HE](1-\chi)\}+k_6[HE](\chi)} = \frac{X_{LI}\ I_a + X_{HE}\ I_a\ (1-\chi)}{k_5\{[LI]+[HE](1-\chi)\}+k_6[HE](\chi)}$$

where χ = fractional deuteration of ϕ-SiD_3 and the other symbols have been defined above.

When [LI] = 0,

$$R_{D_2} = k_8[D][HE](\chi)$$

$$= \frac{k_8[HE](\chi) \quad X_{HE} \; I_a(\chi)}{k_7[HE](1-\chi) + k_8[HE](\chi)}$$

$$= \frac{(\chi)^2 I_a \; k_8}{k_7(1-\chi) + k_8(\chi)} .$$

It is reasonable to assume that $k_7(1-\chi) << k_8(\chi)$ thus $R_{D_2} = (\chi) I_a$. Having solved for χ it is then possible to correct all of the observed values to 100% deuteration.