Supplementary Material Available: Atom labeling schemes and tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles of the compounds 1 and 4 and root-mean-square amplitudes for 1 and least-squares planes for 4 (27 pages); listings of structure factors for 1 and 4 (30 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository numbers CSD 52345 (complex 1) and CSD 52020 (complex 4), the names of the authors, and the journal citation.

Silylene Reactions with Ethylene and Butadiene: Mechanism and Kinetics

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The reactions of SiH_2 (generated from the disilane pyrolysis) with ethylene and with butadiene have been studied by the comparative rate technique. Ethylene trapping of silylene is a consecutive step process involving the formation of a silacyclopropane intermediate which can react back to reactants or forward to either ethylsilylene or vinylsilane. Reaction products of ethylene trapping vary with reaction conditions. At high reactant concentrations and low temperatures the main product is ethylsilane, but numerous other products including diethylsilane and ethyldisilane are also formed. At low reactant concentrations and moderate temperatures the main products are ethylsilane and vinylsilane, while at high temperatures vinylsilane is the only significant product. A number of rate constants and rate-constant parameters for the relevant reactions of the proposed rather complex mechanism have been estimated by using a variety of data sources (including the present paper), and the reaction system has been modeled with reasonable success over a wide range of pressure and temperature conditions.

Introduction

Reactions of silanes with olefins are known to produce the corresponding alkylsilanes; however, under some conditions other products are also produced. Thus Fritz et al.[1] found that silane and ethylene reacted at $T > 380$ °C and atmospheric pressures to produce, in addition to ethylsilane, diethylsilane, triethylsilane, and traces of higher molecular weight products. Rochow and White,[2] in a similar study (456–511 °C) found (besides ethylsilane and diethylsilane) disilane, trisilane, and a product tentatively identified as ethyldisilane. These and other similar results[3,4] were explained in terms of free radical processes (e.g. Scheme I type reactions).

Scheme I. Free Radical Mechanism for Silane–Ethylene Reactions

$$SiH_4 \xrightarrow{1} SiH_3^{\bullet} + H^{\bullet}$$

$$SiH_3^{\bullet} + C_2H_4 \xrightarrow{2} SiH_3CH_2CH_2^{\bullet}$$

$$SiH_3CH_2CH_2^{\bullet} + SiH_4 \xrightarrow{3} SiH_3^{\bullet} + C_2H_5SiH_3$$

$$C_2H_5SiH_3 \xrightarrow{4} C_2H_5SiH_2^{\bullet} + H^{\bullet}$$

$$C_2H_5SiH_2^{\bullet} + C_2H_4 \xrightarrow{5} C_2H_5SiH_2CH_2CH_2^{\bullet}$$

$$C_2H_5SiH_2CH_2CH_2^{\bullet} + SiH_4 \xrightarrow{6} (C_2H_5)_2SiH_2 + SiH_3^{\bullet}$$

etc.

However, it is now clear that silylenes and not free radicals are the dominant intermediates of these reactions and that their mechanism is better represented as shown in Scheme II. Observations which support the Scheme II interpretation are as follows:

Scheme II. Silylene Mechanism for Silane–Ethylene Reactions

$$SiH_4 + (M) \xrightarrow{7} {:}SiH_2 + H_2 + (M)$$

$${:}SiH_2 + C_2H_4 \xrightarrow{8} C_2H_5\ddot{Si}H$$

$$C_2H_5\ddot{Si}H + SiH_4 \xrightarrow{9} C_2H_5SiH_2SiH_3$$

$$C_2H_5SiH_2SiH_3 \xrightarrow{10} C_2H_5SiH_3 + {:}SiH_2$$

$$C_2H_5\ddot{Si}H + C_2H_4 \xrightarrow{11} (C_2H_5)_2Si{:}$$

$$(C_2H_5)_2Si{:} + SiH_4 \xrightarrow{12} (C_2H_5)_2SiHSiH_3$$

$$(C_2H_5)_2SiHSiH_3 \xrightarrow{13} (C_2H_5)_2SiH_2 + SiH_2{:}$$

etc.

(1) Silane–olefin reaction only occur at temperatures where silane itself thermally decomposes.[1]

(2) Silane–olefin reactions have rates that are very comparable to those of the initial step of the silane pyrolysis, inferring an initiation of the former by the latter.[5]

(3) The major initiation reactions of silane and alkylsilane pyrolyses are 1,1-H_2 elimination reactions producing silylenes.[6]

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* To whom reprint requests should be addressed.

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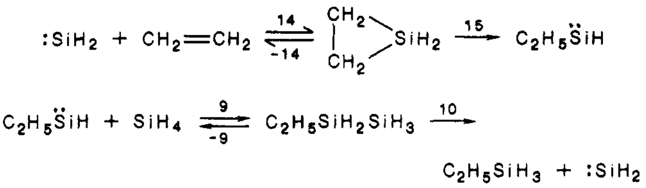
Scheme III. Consecutive Step Mechanism of Silylene Addition to Ethylene To Produce Ethylsilane in Presence of Silane



(4) Silane loss rates in the silane–propylene reaction correlate with propylsilane formation rates;[5] both rates exhibit the same total pressure dependence as the initiation reaction of the silane decomposition (i.e. reaction 7).[5] The latter is known to be a unimolecular reaction in its pressure fall-off regime. This confirms the link between silylene production rates and olefin–silane reaction rates.

(5) Alkylsilylenes (R > CH_3) decompose readily to silylene and the corresponding olefin; hence the inverses of these reactions (e.g. reactions 8 and 11) are reasonable processes.[6]

(6) No ethane is produced in the silane-1-pentene reaction.[5] This argues against a free radical mechanism like Scheme I [i.e. the 1-silyl-2-pentyl radical produced in a reaction like 2 at reaction temperatures would decompose to ethyl (and hence give ethane) before reacting in accord with reactions like 3 to give pentylsilane].

The questions that remain unanswered about silane–olefin reactions concern the mechanistic and kinetic details of reactions like 8 and 11. Are they single-step concerted processes (in which case reactions 8 and 11 would be appropriate representatives) or do they proceed stepwise with the formation of a silacyclopropane intermediate as shown in Scheme III? What are the rate constants and rate constant parameters of the relevant steps? How do silylene trapping rates with ethylene compare to silylene trapping rates with other substrates? These are the questions addressed in this work.

The reaction system studied was the thermal decomposition of disilane (the silylene source) in the presence of butadiene (the reference trapping agent) and ethylene. Three different experimental techniques covering wide ranges of temperature and reactant concentration were employed: static (S), stirred flow (SF),[7] and single pulse shock tube (SPST).[8] The static system thermal decomposition of disilane in the presence of ethylene alone was also studied for the purpose of confirming the product reports of the former silane–ethylene studies.

Experimental Section

Disilane was prepared by $LiAlH_4$ reduction of hexachlorodisilane: Ethylene (Matheson, C. P.) and 1,3-butadiene (Matheson, Instrument purity) were used without further purification. Reactant mixtures exployed in the various studies were as follows: stirred flow (1.00% Si_2H_6, 1.02% C_4H_6, 10% C_2H_4 in argon), shock tube (0.300% Si_2H_6, 0.300 C_4H_6, 2.987% C_2H_4 in argon), static reactor (no. 1, 25% Si_2H_6, 75% C_2H_4; no. 2, 20% Si_2H_6, 20% C_4H_6, 60% C_2H_4). Reaction conditions were as follows: stirred flow, $P_{\text{total}} = 8 \pm 0.8$ Torr, $\tau_{\text{residence}} = 49 \pm 7$ s, $T_{\text{range}} = 674\text{–}715$ K; shock tube, $P_T = 2520 \pm 354$ Torr, $\tau_{\text{residence}} = 320 \pm 50$ μs, $T_{\text{range}} = 935\text{–}987$ K; static reactor, $P = 20$ Torr, $T = 600$ K, conversion range (DS loss) 24–70%. Product separation and analyses for the stirred flow and shock tube studies were made by GSC on a $^1/_4$ in. × 6 ft Porapak Q (100/200 mesh) glass column utilizing a temperature programmed Varian 3700 FID chromatograph coupled to a Hewlett-Packard 3390 A integrator. Product analysis for the static system studies was significantly enhanced by replacing the Porapak Q column (from which high molecular weight products did not properly elute) with a 60 m × 0.75 mm wide bore capillary column coated with a 5-μm SPB-1 film. A recently acquired gas chromatography–mass spectrometry instrument aided in product identification.

Table I. Competitive Rate Data on Silylene Trapping by Ethylene and Butadiene[a–c]

A. Stirred Flow Reactor

T, K	(SCP/VS)[d]	(ES/VS)[d]	$[C_2H_4]/[C_4H_6]$[e]	Y(SCP)[f]	Y(VS)[f]
674.4	1.11	0.65	15.4	0.048	0.039
674.7	1.21	0.68	13.9	0.048	0.037
676.2	1.15	0.67	13.9	0.050	0.045
700.0	1.64	0.64	15.0	0.045	0.043
708.8	1.31	0.59	20.7	0.047	0.041
714.8	2.18	0.65	17.8	0.056	0.048

B. Single Pulse Shock Tube

T, K	(SCP/VS)[d]	(ES/VS)[d]	$[C_2H_4]/[C_4H_6]$[e]	Y(SCP)[f]	Y(VS)[f]
935	4.12		9.92	0.104	0.025
939	3.96		9.92	0.095	0.024
951	4.15		10.1	0.110	0.026
960	5.62		10.1	0.180	0.032
987	7.69	0.18[e]	10.6	0.322	0.041

C. Static Reactor ($T = 600$ K)

time, min	Y(SCP)[f]	(SCP/ES)[d]	% DS conversion
5.0	0.037	6.5	24.2
10.0	0.033	4.5	42.3
20.0	0.033	2.1	68.3

[a] Stirred flow reaction mixture: 1.00% Si_2H_6, 1.02% C_4H_6, 10% C_2H_4 in argon; $P_T = 8$ Torr. [b] Single pulse shock tube reaction mixture: 0.30% Si_2H_6, 0.30% C_4H_6, 2.99% C_2H_4 in argon; $P_T = 2300$ Torr. [c] Static reaction mixture: 20% Si_2H_6, 20% C_4H_6, 60% C_2H_4; $P_T = 20$ Torr. [d] Product mole ratios: SCP, silacyclopentene; VS, vinylsilane; ES, ethylsilane. [e] Average concentrations of ethylene and butadiene in the reacting systems. [f] Product yields as moles of product per mole of disilane reacted. ES was detected but the peak was too small to determine quantitatively.

Results

Product yield data on the disilane decomposition inhibited by ethylene and butadiene for the stirred flow system (SF, $P_T \simeq 8$ Torr, 674–715 K), shock tube system (SPST, $P_T \simeq 2300$ Torr, 935–987 K), and static system (S, $P_T \simeq 20$ Torr, 600 K) are given in Table I, parts A B, and C, respectively.

The only products found in the SF and SPST studies were ethylsilane (ES), silacyclopentene (SCP), and vinylsilane (VS). Yields were all quite low, with totals ranging from 10–15% in the SF studies to 13–35% in the SPST studies. This suggests a high level of polymerization and/or other loss to the walls of high molecular weight species not observable by our GSC methods.

Major products of the static studies of disilane (DS) in C_4H_6 and C_2H_4 were ES and SCP. Vinylsilane was not observed. Improved analytical capabilities revealed the presence of at least six other minor products with a total yield less than 3%. Of these, trisilane (0.3%) and ethyldisilane (<0.1%) were identified. A third, possibly diethylsilacyclopentene (on the basis of its retention time), was produced in the largest yield (~1.3%).

The static system reaction of disilane in the presence of ethylene alone produced mainly ethylsilane in yields which increased in time. Yield data are shown in Table IIA. Up to 17 other products were detected, the most important of which were identified as diethylsilane (in

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(6) Ring, M. A.; O'Neal, H. E.; Rickborn, S. F.; Sawrey, B. A. *Organometallics* **1983**, *2*, 1891.

(7) Rickborn, S. F.; Rogers, D. S.; Ring, M. A.; O'Neal, H. E. *J. Phys. Chem.* **1986**, *90*, 408.

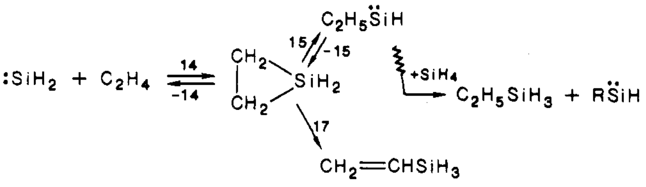
(8) Newman, C. G.; O'Neal, H. E.; Ring, M. A.; Leska, F.; Shipley, N. *Int. J. Chem. Kinet.* **1979**, *11*, 1167.

Table II. Disilane Decomposition in the Presence of Ethylene (600 K, Static Reactor)[a]

	yields × 10^2									
t, min	ES	VS	E2S	EDS	TS	E2DS	E2VS	ETS	E2TS	% CONV
	A. Product Yields[b] (Experimental Determination)									
10	1.3		1.1	0.3	0.4		3.3[c]		0.5[d]	57
20	3.2	0.10	2.4	0.6	0.7		3.0		0.6	82
60	9.5	0.14	6.3	1.0	0.9		6.0		1.3	99
	B. Product Yields Predicted (by the Modeling)[b]									
10	0.88	0.04	1.1	1.0	26.2	2.0	6.1	4.5	5.6	36
20	1.8	0.05	2.7	1.6	20.4	3.8	8.1	3.1	4.3	57
60	5.2	0.07	11.5	1.8	6.6	6.3	14.9	0.7	1.1	88

[a] Static system reaction mixture: 25% DS, 75% C_2H_4; P_{total} = 20 Torr. [b] For product identification see Table III footnotes. [c] Sum of all products in this molecular weight range as determined from the sums of the GSC peak areas. [d] Product with similar molecular weight at E2TS, but not yet identified.

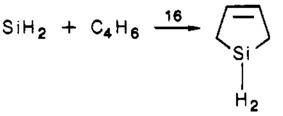
Scheme IV. Extended Scheme III



yields comparable to ethylsilane) and ethyldisilane and trisilane (in yields less than 1%). Only one of the remaining 14 (possibly diethyldisilane or diethylvinylsilane) was produced in yields comparable to ES. Vinylsilane *was* formed, but in yields 30–100 times smaller than those of ES. Thus our static system results for the disilane–ethylene reaction confirm in all essential points the reports of prior studies on the silane–ethylene reaction.

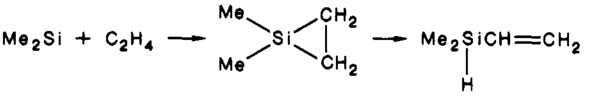
Discussion

Ethylsilane and silacyclopentene are the silylene trapping products of ethylene (reactions 14 and 15) and of butadiene (reaction 16), respectively; hence their presence



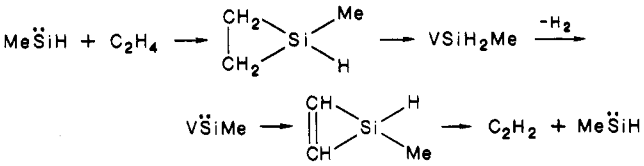
in the products of all three reaction systems was expected. However, the large yields of VS found in the SF and SPST studies was at first very surprising, particularly as VS was not a reported product of the earlier studies. Production of VS, however, follows logically from an extension of Scheme III, and in this sense gives evidence for that scheme. Thus silacyclopropane, formed by direct addition of silylene to the π system of ethylene in reaction 14, can ring open by 1,2-H migrations in two ways: (1) H migration from Si to C (as in reaction 15) leading eventually via the reactions of ethylsilylene and silane to ES (reactions 9 and 10) or (2) H migration from C to Si (reaction 17) leading directly to vinylsilane. This is shown in Scheme IV below. That silacyclopropanes can react to vinylsilanes as in reaction 17 was demonstrated by Skell[9] through a study of the reaction of dimethyldichlorosilane with Na–K vapor. The reaction can be described as

$$Me_2SiCl_2 + 2Na \rightarrow 2NaCl + Me_2Si$$

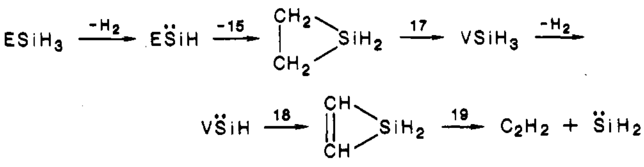


Skell was able to estimate an upper limit of 0.1 s for the half-life of the dimethylsilacyclopropane intermediate at 543 K.

Alkylsilanes with R > CH_3 are known to decompose readily to silylene and the corresponding olefin; therefore reaction 15 is reversible.[6] The favored reaction product of silane–olefin reactions, then, will depend strongly on reaction conditions. VS will be favored over ES by low reactant concentrations (as used in the SF and SPST reaction systems) since reaction 17 to VS is unimolecular while reaction 9 to ethylsilane is dependent on SiH_4 (or disilane) concentration. Also, VS will be favored by high temperatures since $(\Delta H^\circ_{-15,15} + E_{17}) > E_9$ (i.e. there is a Le Chatelier shift with increasing temperature of ethylsilylene toward VS). The experimental observations correlate with these expectations (see ES/VS yield ratios of Table I), and this is, as stated previously, strong support for the Scheme III consecutive step mechanistic interpretation of silane–olefin reactions. Similar schemes have been proposed by us to explain the products and reaction kinetics of related reaction systems. Thus the enhanced production of acetylene with added ethylene in the SPST decomposition of methylsilane[10] was rationalized by the reaction sequence



Also, the small yields of vinylsilane and acetylene found in the SPST decomposition of ethylsilane[11] were explained by the reactions



Reaction Modeling. Modeling of the disilane decomposition in the presence of ethylene and butadiene, or in the presence of ethylene alone, was done in terms of the mechanism shown in Table III. The basic reactions are the silylene (SiH_2) trapping reactions with ethylene and butadiene (14–17), but the mechanism has been extended to include analogous processes for other silylene intermediates (e.g. ethylsilylene, diethylsilylene, and silylsilylene). Arrhenius parameter assignments were made

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[9] Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 1442.

[10] Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D. *Int. J. Chem. Kinet.* **1984**, *16*, 7.

[11] Rickborn, S. F.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1984**, *16*, 1371.

Table III. Mechanism Employed in the Reaction Modeling[a]

	log *A*	*E*, kcal	ref
$Si_2H_6 \xrightarrow{20} SiH_4 + SiH_2$	14.41[b]	47.59[b]	20
$\xleftarrow{-20}$	10.82	0.00	14
$SiH_2 + BD \xrightarrow{16} \underline{SCP}$	11.02	1.83	14, 17, 26
$SiH_2 + C_2H_4 \xrightarrow{14} A$	10.80	0.00	14
$\xleftarrow{-14}$	16.61	30.00	see text
$ESiH \xrightarrow{-15} A$	12.85	18.45	see text
$\xleftarrow{15}$	14.40	19.20	see text
$A \xrightarrow{17} \underline{VS}$	13.50	24.30	see text
$ESiH + Si_2H_6 \xrightarrow{21} \underline{ETS}$	11.00	1.70	see text
$\xleftarrow{-21}$	14.50	49.00	7
$ETS \xrightarrow{22} SiH_3SiH + \underline{ES}$	14.50	49.00	7
$ESiH + SiH_4 \xrightarrow{9} \underline{EDS}$	10.30	1.70	see text
$\xleftarrow{-9}$	14.10	49.90	7
$EDS \xrightarrow{10} SiH_2 + \underline{ES}$	15.30	50.80	24
$ESiH + BD \xrightarrow{23} \underline{ESCP}$	10.70	4.00	see text
$ESiH + C_2H_4 \xrightarrow{24} C$	10.90	1.70	see text
$\xleftarrow{-24}$	16.61	30.00	see text
$C \xrightarrow{25} \underline{EVS}$	13.50	24.30	see text
$E_2Si: \xrightarrow{26} C$	12.85	18.90	see text
$\xleftarrow{-26}$	13.90	18.50	see text
$E_2Si: + Si_2H_6 \xrightarrow{27} E_2TS$	10.20	4.00	see text
$\xleftarrow{-27}$	14.20	49.00	7
$E_2TS \xrightarrow{28} SiH_2 + E_2DS$	15.30	50.80	7
$E_2TS \xrightarrow{29} SiH_3SiH + E_2S$	14.50	49.00	7
$E_2Si: + C_2H_4 \xrightarrow{30} B$	10.60	4.00	see text
$\xleftarrow{-30}$	16.61	30.00	see text
$B \xrightarrow{31} E_2VS$	13.50	24.30	see text
$E_2Si: + BD \xrightarrow{32} E_2\underline{SCP}$	10.30	4.00	see text
$E_2Si + SiH_4 \xrightarrow{33} E_2DS$	10.30	3.85	see text
$\xleftarrow{-33}$	14.10	49.90	7
$E_2DS \xrightarrow{34} SiH_2 + E_2S$	15.30	50.80	7
$ETS \xrightarrow{35} SiH_2 + \underline{EDS}$	15.30	50.80	7
$SiH_2 + Si_2H_6 \xrightarrow{36} Si_3H_8$	11.53	0.00	14
$\xleftarrow{-36}$	15.69	53.00	7
$Si_3H_8 \xrightarrow{37} SiH_3SiH + SiH_4$	14.68	49.20	24
$\xleftarrow{-37}$	10.30	1.70	from thermochem
$VS \xrightarrow{38}$ products	15.0	52.0	27
Sink Reactions			
$SiH_3SiH \xrightarrow{39} Si_2H_4$	12.8	3.0	13
$\xleftarrow{-39}$	13.7	26.3	13
$Si_2H_4 \xrightarrow{40} SiH_2Si + H_2$	14.0	35.0	13
$Si_2H_6 \xrightarrow{48} X + H_2$	14.40	52.2	12
$Si_3H_8 \xrightarrow{49} X + H_2$	14.40	52.2	12
$EDS \xrightarrow{50} X + H_2$	14.10	52.2	12
$ETS \xrightarrow{51} X + H_2$	14.10	52.2	12
where X is a silylene polymer $(SiH_2)_n$			

[a] BD = butadiene; SCP = silacyclopentene, A = silacyclopropane, VS = vinylsilane, ETS = ethyltrisilane, ES = ethylsilane, EDS = ethyldisilane, ESCP = ethylsilacyclopentene, C = ethylsilacyclopropane, EVS = ethylvinylsilane, E2TS = diethyltrisilane, E2DS = diethyldisilane, E2S = diethylsilane, B = diethylsilacyclopropane, E2VS = diethylvinylsilane, E2SCP = diethylsilacyclopentene, D = silylsilacyclopropane, X denotes any disilene (>Si=Si<), monomer or polymer. [b] For the static decompositions $\log k_{20} = 15.13 - 50.92/RT$.

from available data, by analogy with available data, or through thermochemical kinetic estimtes based on pertinent experimental observations (see next section).

A major problem in the modeling concerns the nature of the sink reactions. In prior modeling studies gas-phase silylene polymerizations with eventual loss to the walls were assumed to be the major channels for reaction species removal.[12] In this paper we have explored another possibility inspired by a recent paper by Ho et al. on the thermodynamics of Si_2H_n species and on their calculated activation energy for the $SiH_3SiH \rightarrow SiH_2{=}SiH_2$ isomerization.[13] Their calculations indicate that reactions 39 and 40 can serve as a very effective silylene sink with SiH_2Si as a polymerizable product. We have modeled the disilane–ethylene, butdiene system with both kinds of sink processes and found nearly identical results for the product yields of the observed products. The true nature of the sink reactions, therefore, remains an open question.

Critical Rate Constants and Their Parameter Assignments. (1) The pseudo-first-order rate constant for trapping of ESiH (and E_2Si:) by disilane and silane to form $ESiH_3$ (and E_2SiH_2) can be approximately equated to

$$k_{\text{eff}}(\text{RSi–H}) = k_{21}\left(\frac{b}{1+b}\right)[Si_2H_6] + k_9\left(\frac{a}{1+a}\right)[SiH_4] \qquad \text{(I)}$$

where b is the probability that ETS reacts to form $ESiH_3$, $\simeq 0.25$, a is the probability that EDS reacts to form $ESiH_3$,

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[12] White, R. T.; Espino-Rios, R. L.; Rogers, D. S.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1985**, *17*, 1029.

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$\simeq 0.86$, and $[\overline{Si_2H_6}]$ and $[\overline{SiH_4}]$ are the average concentrations of disilane and silane during a reaction. (Under stirred flow reaction conditions (675 K), $[\overline{Si_2H_6}] \simeq [\overline{SiH_4}] \simeq 9.5 \times 10^{-7}$ M; for the static system reaction (600 K), $[\overline{Si_2H_6}] \approx 8.8 \times 10^{-5}$ M while $[\overline{SiH_4}] \simeq 2.2 \times 10^{-5}$ M. The values of a and b were estimated by using previously suggested generalized Arrhenium parameters which can be shown to fit all available disilane decomposition data within ±15% at study temperatures.[7])

The absolute rate constants for SiH_2[14] and Me_2Si[15] trapping by silane have been measured to be, respectively, 6.6×10^{10} and 1.2×10^{8} M^{-1} s^{-1}. Walsh[16] believes that the surprising difference in rate constants for these species resides in their activation energies and estimates a 3.4 kcal activation energy for the dimethylsilylene reaction (compared to a zero value for silylene). It seems reasonable to assign an intermediate reactivity to the MeSiH reaction with silane; hence $A \approx 5 \times 10^{10}$ M^{-1} s^{-1} and $E \approx 1.7$ kcal. The reactivities of larger monoalkyl-substituted silylenes would be expected to be similar, but perhaps lower on steric grounds, therefore we have assigned parameters for the ethylsilylene reaction with silane of $A_9 = 10^{10.3}$ M^{-1} s^{-1} and $E_9 = 1.7$ kcal. Relative rate studies of silylene reactions toward silane and disilane have found that disilane is the better trap by factors of 4–6. Therefore, we have assigned for the latter reaction, $A_{21} = 10^{11.0}$ M^{-1} s^{-1}. On this basis, eq I gives $k_{eff(ESiH)} \approx 7.8 \times 10^{3}$ s^{-1} for the stirred flow reaction at 675 K and $k_{eff(ESiH)} = 4.7 \times 10^{5}$ s^{-1} for the static system reaction at 600 K.

(2) Relative rate studies of silylene with silane and ethylene[17] and silylene with silane and 1-butene[18] have found similar trapping efficiencies (i.e., the reported rate constant ratios are 1 with ethylene and 2 in favor of the olefin with 1-butene). Since the latter result pertains to the trapping reactions only (i.e., no back reaction of the disilane product), it is in quite good agreement with the factor of 5 estimate obtained here (which includes the back reaction of the disilane).

Thus, at 600 K in the static system we have

$$\frac{k_{24}[C_2H_4]}{k_{eff}[RS\text{-}H]} \simeq \frac{\sum Y(\text{heavy products})}{Y[ESiH_3]} \simeq 5$$

$$[C_2H_4] = 3 \times 10^{-4}\ M$$

Therefore

$$k_{24} \simeq \frac{5 \times 4.7 \times 10^{5}}{3 \times 10^{-4}} \simeq 7.9 \times 10^{9}\ s^{-1}$$

(3) In the static system at relatively high substrate concentrations, it is reasonable to assume that all ethylsilylene formed will be trapped by ethylene, disilane, or silane. Therefore, the ratio of the yields of all trapping products (other than vinylsilane) to that of vinylsilane provides a competitive measure of silacyclopropane reactions to ethylsilylene (reaction 15) and vinylsilane (reaction 17). This ratio was found to be about 150. Therefore

$$\frac{Y(\text{all trapped products})}{Y(VS)} \simeq \frac{k_{15}}{k_{17}} \simeq 150, \text{ at } 600\ K$$

Thermochemical estimates[19] give $A_{15} \simeq 10^{14.2\pm0.3}$ s^{-1} and $A_{17} \simeq 10^{13.5\pm0.3}$ s^{-1}. Hence $(E_{17} - E_{15}) \simeq 4.0 \pm 1.6$ kcal.

(4) At stirred flow temperatures, since substrate concentrations are quite low, ethylsilylene and silacyclopropane establish a near equilibrium. Therefore

$$\left[\frac{Y(ES)}{Y(VS)}\right]_{675\ K} \simeq 0.65 \simeq K_{15,-15}k_{eff}(RSi\text{–}H)/k_{17}$$

With $k_{15}/k_{17} \simeq 100$ at 675 K and $k_{eff}(RSi\text{–}H) = 7.8 \times 10^{3}$ s^{-1} (stirred flow, 675 K) the above reduces to

$$\frac{Y(ES)}{Y(VS)} \simeq 0.65 = \frac{100(7.8 \times 10^{3})}{k_{-15}}$$

Thus, $k_{-15(675K)} \simeq 1.2 \times 10^{6}$ M^{-1} s^{-1}. With $A_{-15} \simeq 10^{12.6}$ s^{-1}, this gives $E_{-15} \simeq 20.1$ kcal.

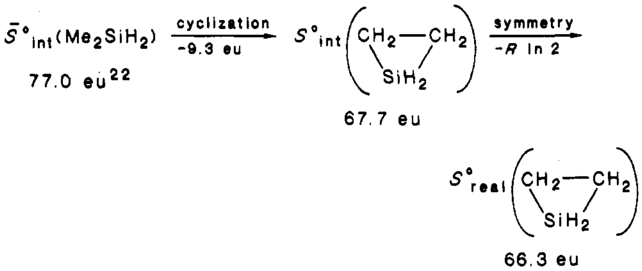
(5) In the shock-induced decomposition of ethylsilane at 1150 K,[11] the observed yields of ethylene vs. vinylsilane and acetylene were about 90% and 6%, respectively. (Acetylene is formed from the subsequent decomposition of vinylsilane.) Assuming that these products arise from ethylsilylene and silacyclopropane via reactions −15 and −14 and −15 and 17, this observation gives

$$\left[\frac{Y(C_2H_4)}{Y(VS)}\right]_{1150\ K} \simeq 15 = \frac{k_{-14}}{k_{17}} \simeq \frac{10^{16.6}}{10^{13.5}}e^{(E_{17}-E_{-14})/RT}$$

From which $(E_{-14} - E_{17}) \simeq 10.1$ kcal.

(6) From the Skell lifetime[9] for the dimethylsilacyclopropane reaction to vinyldimethylsilane (i.e., $t_{1/2} < 0.1$ s, 543 K), with the estimated[19] $A_{17} \simeq 10^{13.5}$ s^{-1} one obtains $E_{17} \leqslant 31.1$ kcal.

(7) In (5) above, an estimated value of $A_{-14} \simeq 10^{16.6}$ s^{-1} was employed. We can check this for consistency with our $A_{14} \simeq 10^{10.80}$ M^{-1} s^{-1} through the reaction entropy which is estimated to be $\Delta S°_{14,-14(298K)} \simeq -35.3$ cal/(deg mol). (Entropy of silacyclopropane is estimated by the difference method (19) with dimethylsilane as model as follows:



With $S°(C_2H_4) = 52.4$ eu/mol[19] and $S°(SiH_2) = 49.2$ eu/mol,[23] this gives $\Delta S°_{14,-14} = -35.3$ eu.)

The reaction A factors give

$$\Delta S_{14,-14(800K)} = R \ln\left[\frac{A_{14}(atm^{-1}\ s^{-1})}{A_{-14}(s^{-1})}\right] = -36.9 \text{ cal/deg}$$

which is certainly an agreement within the errors of the estimates.

(8) Finally, the activation energy estimates obtained above must agree with the overall reaction enthalpy of ethylsilylene decomposition to ethylene and silylene. The

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Table IV. Modeling vs Experimental Results for the Disilane Decomposition under Ethylene and Butadiene Inhibition: Stirred Flow and Shock Tube Reactors and Static System Reactors

Stirred Flow[a,c]

		×10^2				
T, K		Y(SCP)	Y(VS)	Y(ES)	(SCP/VS)	(ES/VS)
675	exptl	4.8	4.0	2.5	1.16	0.66
	calcd	9.53	8.37	5.93	1.14	0.71
715	exptl	5.6	4.8	3.1	2.18	0.65
	calcd	15.32	5.93	3.79	2.58	0.64

Shock Tube[b,d]

		×10^2				
T, K		Y(SCP)	Y(VS)	Y(ES)	(SCP/VS)	(ES/VS)
935	exptl	10.4	2.5		4.12	
	calcd	9.34	2.25	0.58	4.16	0.26
950	exptl	11.0	2.6		4.15	
	calcd	12.15	2.66	0.80	4.58	0.30
987	exptl	32.2	4.1	0.74	7.69	0.18
	calcd	21.46	3.12	1.31	6.87	0.42

Static Reactor (T = 600 K)

time, min		Y(SCP)	(SCP/ES)	% conversion	TS[e]	EDS	E$_2$SCP
5.0	exptl	0.037	6.5	24.2			
	calcd	0.0248	6.11	19.0	29.8	0.55	5.7
10.0	exptl	0.033	4.5	42.3			
	calcd	0.0274	3.3	33.8	26.4	1.0	6.7
20.0	exptl	0.033	2.1	68.3	0.3	0.1	(1.3?)
	calcd	0.033	1.94	54.5	20.4	1.5	8.5

[a] Other products predicted with significant yields (i.e., over 1% yield) are ethylsilacyclopentene (~3-4), H$_2$ (~8%) vinylethylsilane (~3%), and products of ESiH$_2$SiH (~20-25%). Trisilane is also predicted at 675 K (~10%). [b] Other products predicted with yields above 1% are ethylsilacyclopentene (~1-2%), trisilane (~20%), hydrogen (~8%), and products of ESiH$_2$SiH (~8%). [c] Reaction mixture: Si$_2$H$_6$ = C$_4$H$_6$ = 1.0%, C$_2$H$_4$ = 10% in argon; residence time, 30 s; P_{total} = 8.0 Torr. [d] Reaction mixture: Si$_2$H$_6$ = C$_4$H$_6$ = 0.30%, C$_2$H$_4$ = 2.99% argon; residence time, 300 μs; P_{total} = 2520 Torr. [e] Note the very high yields of TS predicted by the modeling.

enthalpy of this reaction, on the basis of recent heat of formation evaluations on silylene (ΔH°_f = 64.3 kcal/mol)[20] and ethylsilylene (ΔH°_f = 46.1 kcal/mol),[21] is about 30.7 kcal/mol. Our final modeling ($\Delta H^\circ = (E_{-14} + E_{-15}) - (E_{14} + E_{15})$ gives 29.25 kcal/mol.

In summary, the following assignments have been deduced: (1) $(k_{15}/k_{17})_{600K} \simeq 150$, $(E_{17} - E_{15}) = 4.0 \pm 1.6$ kcal; (2) $k_{-15(675K)} \simeq 1.2 \times 10^6$ s^{-1}, $E_{-15} \simeq 20.1$ kcal; (3) $(k_{-14}/k_{17})_{1150K} \simeq 15$, $(E_{-14} - E_{17}) \simeq 10.1$ kcal; (4) $E_{17} \leq 31.1$ kcal for $A_{17} \simeq 10^{13.5}$ s^{-1}. The Arrhenius parameters used in the modeling and shown in Table III are, with the exception of (3) above, generally consistent with these deductions although minor adjustments of a few kilocalories in E and factors of about 2 in A were made in some reactions to improve the modeling fits.

Modeling Results. Results of the modeling for the disilane decomposition in the presence of ethylene and butadiene (SF, SPST, and S conditions) are given in Table IV. Results for the DS decomposition in the presence of ethylene alone (S conditions) are given in Table IIB. While absolute product yield predictions are generally too high, product yield ratios of the major products are in good agreement with the observations. Thus the trends in the (SCP/VS) and (ES/VS) yield ratios with temperature and reactant concentrations of the SF and SPST studies agree well with the experimental observations, as do the variations in time of the (SCP/ES) ratios of the static system studies. It is also very interesting to note that no products of great importance besides those observed (with the exception of trisilane and diethylsilacyclopentene in the static system with butadiene and trisilane and some heavy products in the static system without butadiene) are predicted by the modeling. These correlations tend to confirm the essential features of the proposed mechanism. The reactions studies are far too complex to be able to establish through the modeling accurate Arrhenius parameters for any of the relevant reactions. One can only conclude, from the favorable agreements between observation and modeling for the main products, that the rate constants employed for the Scheme III reactions are relatively self-consistent. That absolute product yield predictions are not particularly good indicates that other as yet unknown silylene sink reactions of real importance exist. Overestimation, by the modeling, of yields for the higher molecular weight products (i.e. those formed after two or more trapping reactions with the substrates (C$_2$H$_4$, C$_4$H$_6$, Si$_2$H$_6$ and SiH$_4$)) is also evidence for additional scavenging reactions. The very high yields of trisilane predicted by the modeling for the static reaction (as opposed to the rather modest yields actually observed) poses an interesting problem. In a reexamination of the kinetics of the static system decomposition of trisilane[24] we have found that trisilane loss rates are about a factor of two faster than the sum of the product (SiH$_4$, Si$_2$H$_6$ and H$_2$) formation rates.[25] Therefore, there is solid evidence for important trisilane reaction channels not currently recognized. This is an important problem waiting resolution.

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Registry No. ES, 2814-79-1; SCP, 7049-25-4; VS, 7291-09-0; H$_3$SiSiH$_3$, 1590-87-0; CH$_2$=CH$_2$, 74-85-1; CH$_2$=CHCH=$_2$, 106-99-0; (C$_2$H$_5$)$_2$SiH$_2$, 754-91-6; C$_2$H$_5$SiH$_2$SiH$_3$, 7528-37-2; H$_3$SiSiH$_2$SiH$_3$, 7783-26-8; H$_2$Si:, 13825-90-6.

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