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Kinetic and Product Studies of the Thermal Decomposition of Dimethylsilane in a Single-Pulse Shock Tube and in a Stirred Flow Reactor

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Kinetic and product studies of the pyrolyses of dimethylsilane in a single-pulse shock tube (1135–1290 K) and in a stirred flow reactor (890–1000 K) are reported. The shock-induced reaction is accelerated by free-radical and silylene chains which cannot be quenched by trapping agents. The mechanisms of the pyrolyses in various temperature ranges are discussed and modeling results for the stirred flow and shock tube reactions are shown to be in reasonable agreement with experimental observations. Mechanisms for the decomposition of dimethylsilylene to ethylene and acetylene via silacyclopropane and silacyclopropene intermediates, respectively, are proposed. Arrhenius parameters for molecular elimination of methane from dimethylsilane are deduced ($\log k_{CH_4} = 14.8 - 73.000/2.3RT$), establishing an activation energy for CH_3SiH insertion into the (C–H) bond of methane of $E \simeq 24.5$ kcal (pressure standard state).

Introduction

The decomposition of dimethylsilane (DMS) has previously been studied statically between 717 and 773 K by Neudorfl and Strausz (NS).[1] At conversions below 0.5% the major products were H_2 and 1,1,2,2-tetramethyldisilane. Minor products were methylsilane and trimethylsilane with traces of polymer. Rates were inhibited by additions of ethylene, and kinetics under inhibition were attributed to the "usual" three-center hydrogen elimination reaction:

$$Me_2SiH_2 \xrightarrow{1} Me_2Si: + H_2$$

$$k_{1(NS)} = 10^{14.3}e^{-68000\pm1000/RT}\ s^{-1}$$

The studies reported here, conducted in a single-pulse shock tube (temperature range 1135–1290 K) and a stirred flow reactor (temperature range 890–1000 K), were initiated for several reasons. First, shock tube data coupled with stirred flow and static system data cover a temperature range of almost 600 K; hence very good Arrhenius parameters for the decomposition should in principle be realized. Second, through higher temperature studies we hoped to investigate the kinetics of unimolecular methane elimination and 1,2 hydrogen elimination from dimethylsilane. Similar primary dissociation reactions have been documented at shock temperatures for several monoalkylsilanes.[2-6] Finally, from the overall decomposition kinetics of dimethylsilane we hoped to learn more about the silylene chain reactions which appear to contribute to the decomposition of other substituted silanes (e.g., vinylsilane,[4] propylsilane,[5] and ethylsilane[6]).

Experimental Methods

Dimethylsilane was prepared by $LiAlH_4$ reduction of the corresponding chloride supplied by Petrarch Chemicals. Product identification was done by GLC retention times, by infrared spectra (with a Perkin Elmer 337 IR spectrophotometer), and by mass spectra (with a Hitachi Perkin-Elmer RNU-6E mass spectrometer). The shock tube apparatus and comparative rate technique employed have been described previously.[7] The comparative rate standard employed was cyclopropane. Products, drawn from the end plate, were analyzed on a $^1/_8$ in. × 4 ft Porapak N (150–200 mesh) column in a Varian 1400 GLC programmed from 60 to 180 °C.

TABLE I: Arrhenius Parameters for the Loss of Dimethylsilane in the Absence and Presence of Inhibitors (Shock Tube Study Results)

mixture[a]	log *A*, s^{-1}	E_{act},[b] cal/mol	temp range, K	no. of points
A	14.30	68000 ± 1000	713–773	ref 1
B	12.35	52297 ± 5468	1196–1269	15
C	13.34	59622 ± 6378	1188–1280	11
D	14.24	63699 ± 9064	1145–1286	12
E	14.36	64520 ± 5840	1135–1252	5

[a] Reaction mixtures and their compositions are as follows: (B) 0.1% each of $(Me)_2SiH_2$, Δ, and Xe; 99.7% Ar; (C) 1.0% $(Me)_2SiH_2$, 0.5% Δ; 98.5% Ar; (D) 0.1% each of $(Me)_2SiH_2$, Δ, C_2H_6, Xe; 3.0% toluene-d_8, 96.6% Ar; (E) 0.1% each of $(Me)_2SiH_2$, Δ, C_2H_6; 3.0% 1,3-butadiene, 96.7% Ar. [b] Errors are for the 95% confidence limits.

The stirred flow study was made in a 64-cm^3 quartz reactor surrounded by an aluminum block air bath furnace heated resistively. Reaction mixtures, 10% dimethylsilane in nitrogen, were passed through the reactor at total flow rates and reaction pressures of 0.25 ± 0.06 μmol/s and 6.8 torr, respectively. Temperatures were measured by a calibrated Doric Instruments Trendicator, Model 410A, and product analyses were made on the same Porpak N column but with a Varian FID (Model 3700) GLC equipped with a Hewlett-Packard digital integrator (Model 3390A). The stirred flow apparatus and method as applied to our apparatus were checked via kinetic studies of the decompositions of cyclopropane and cyclopentene. Conditions were as follows: 6.3% cyclopentene and 11.8% cyclopropane in nitrogen, total flow rates in the range 51 ± 30 μmol/s, residence times from 19 to 45 s, and temperatures from 809 to 912 K. Both reactions (I and II) are known[8] to proceed cleanly and unimolecularly. Our

(I)

$$k_I = 10^{13.04}e^{-58800/RT}\ s^{-1}$$

(II)

$$k_{II} = 10^{15.20}e^{-65500/RT}\ s^{-1}$$

calibration studies gave rate constants in very good agreement with these literature values. Thus we obtained $k(c\text{-}C_5H_8) = 10^{13.28}e^{-59775\pm136.4/RT}\ s^{-1}$ and $k(\Delta) = 10^{15.36}e^{-66490\pm1516/RT}\ s^{-1}$, where the errors shown correspond to the 95% confidence limit.

Kinetic Results

Several shock tube comparative rate studies were made. In some, DMS was pyrolyzed in the presence of chemically inert

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TABLE II: Product Yield Data from the Shock-Induced Decomposition of Dimethylsilane

		yield								
reaction[a] mixture	% decompn	CH_4	C_2H_6	C_2H_4	C_2H_2	H_2	$MeSiH_3$	Me_3SiH	C_6H_6	C
B	16–20	0.48	0.17	0.34	0.19	1.0				1.88
	20–30	0.43	0.15	0.30	0.17					1.67
	40–50	0.43	0.14	0.32	0.22					1.79
	50–60	0.44	0.14	0.33	0.24	1.12				1.86
C	10–16	0.46	0.036	0.18	0.085		0.036	0.047		1.21
	25–30	0.43	0.031	0.18	0.085		0.038	0.041		1.21
	39–47	0.46	0.028	0.19	0.106		0.033	0.046		1.28
	62	0.47	0.028	0.22	0.130		0.020	0.051		1.40
D	3–10	1.07[b]		0.43[b]	0.23[b]				0.71[b]	2.39[b]
	12	1.49		0.59	0.38				1.09	3.43
	23–26	1.36		0.53	0.51				0.90	3.44
	42–64	1.65		0.66	0.92				1.06	5.46
E	3–10	1.27[b]		5.20[b]	3.68[b]					
	20	1.42		5.70	4.73					
	36	1.57		6.19	5.46					

[a] Reaction mixture compositions are given in Table I. [b] These excess product yields have been enhanced by the decomposition of trapping reagents (toluene and butadiene).

species (e.g., argon carrier and the internal standards Xe, Δ, etc.), and in others the DMS was pyrolyzed in the presence of trapping reagents, namely, toluene and 1,3-butadiene. The reactant mixture compositions, the temperature ranges studied, and the resulting Arrhenius parameters for DMS loss are shown in Table I.

The large errors in the rate parameters of the various mixtures are indicative of reaction complexities. Thus similar errors were observed in other shock-initiated uninhibited pyrolyses of alkylsilanes (e.g., vinylsilane,[4] propylsilane,[5] and ethylsilane[6]). However, in the presence of butadiene (or acetylene) these latter systems exhibited much better behaved kinetics. The interpretation was that butadiene scavenged the silylene intermediates which otherwise propagated short-chain reactions and produced erratic kinetic results. By contrast, attempts to quench chain reactions in DMS through additions of either toluene (a good free radical trap) or butadiene (a good silylene trap) achieved only limited success. This is apparent from the Figure 1 relative rate plots of mixtures B and C (uninhibited DMS), mixture D (added toluene), mixture E (added butadiene), and mixture A (NS extrapolated kinetics). All of our shock tube systems produced rates at least five times greater than those predicted by the NS parameters. In addition, the trapping agents did little to either reduce the rates or improve the errors in the rate data. The implication is that both silylene and free-radical chain processes occur in the DMS shock tube pyrolysis and that these chain processes are not much suppressed by trapping agents. A number of observations support this thesis. Thus while toluene is an excellent free-radical trap at low temperatures, it can be a reasonably good radical source at high temperatures.[9-11] The reactions involved are $PhCH_3 \rightarrow PhCH_2\cdot + H\cdot$ and $H\cdot + PhCH_3 \rightarrow PhH + CH_3\cdot$, and the production of benzene in our mixture D studies is evidence for the occurrence of these reactions. Also, at temperatures above 1200 K, benzyl radicals can propagate chain reactions,[11] and silacyclopentenes (the trapping products of silylenes and butadiene) are relatively unstable.[9] There is therefore good reason to believe that the inhibited DMS pyrolysis at shock tube reaction temperatures is not maximally inhibited. In the unlikely event, however, that our shock tube experimental kinetic parameters of the DMS inhibited systems represented the maximally inhibited reaction and therefore the observed parameters were reasonable measures of the primary dissociation reactions, we initiated lower temperature stirred flow kinetic studies of the pyrolysis. A systematic curvature in the Arrhenius plot of the DMS pyrolysis toward higher rates at higher temperatures would be evident from the combined data (stirred flow and shock tube) if this were the case.

The results of our stirred flow kinetic study (covering the range 865–991 K) showed no evidence of rate increases above the NS predicted rates. The Arrhenius parameters obtained for DMS loss, $\log k = 13.96 \pm 0.76 - 66990 \pm 3250\ \mathrm{cal}/2.303RT$, are, within the experimental errors, in good agreement[26] with those of NS. Therefore, the enhanced rates at shock temperatures are caused by unquenched silylene and free radical chain processes. Assuming that the NS extrapolation of curve A (Figure 1) is valid, one finds that the primary process reactions of DMS account for less than 15% of the observed reaction. The remaining 85% reaction is chain induced.

Shock-Initiated Reaction, Product Yield Data, and Their Mechanistic Implications. Pertinent product yield data (based on dimethylsilane loss) from the shock tube studies are tabulated in Table II.

While molecular methane elimination (reaction 2) is expected

$$\mathrm{DMS} \xrightarrow{2} CH_4 + CH_3SiH$$

to be an important primary dissociation reaction of DMS at shock temperatures,[27] since up to 85% of the reaction is chain produced, the high methane yields observed must arise mainly from a chain source. The most reasonable is the methyl radical chain of Scheme I. The appearance of ethane in the products supports this interpretation. Increases in the yield ratios ($Y(CH_4)/Y(C_2H_6)$) for runs 0.1% in DMS (mixture B) and 1.0% in DMS (mixture C) are about a factor of 5; Scheme I predicts a ratio increase of $10^{1/2} \simeq 3.2$, a reasonable agreement.

SCHEME I: Methyl Radical Chain in DMS Pyrolysis[28]

$$\mathrm{DMS} \xrightarrow{3} CH_3\cdot + MeSiH_2\cdot$$

$$CH_3\cdot + Me_2SiH_2 \xrightarrow{4} Me_2SiH\cdot + CH_4$$

$$Me_2SiH\cdot \xrightarrow{8} MeSiH: + CH_3\cdot$$

$$MeSiH + \mathrm{DMS} \xrightarrow{18} [MeSiH_2SiHMe_2] \xrightarrow{25} Me_2Si: + MeSiH_3$$

$$MeSiH_3 \xrightarrow{61} MeSiH + H_2$$

$$CH_3\cdot + CH_3\cdot \xrightarrow{14} C_2H_6$$

Carbon mass balance comparisons in mixtures B and C provide evidence for silylene processes. About 90% of the carbon is accounted for in the products of the mixture B (0.1% DMS) runs. However, at tenfold higher reactant levels (mixture C, 1.0% DMS), carbon mass balances decreased substantially. This material loss is consistent with previous monosilane decomposition systems[3-6] and arises from disilene polymerizations and decom-

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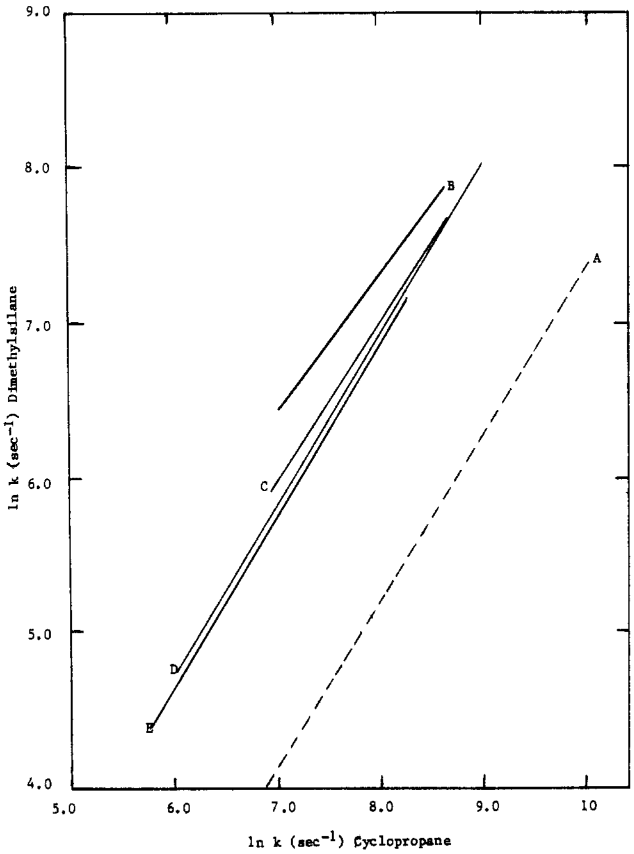
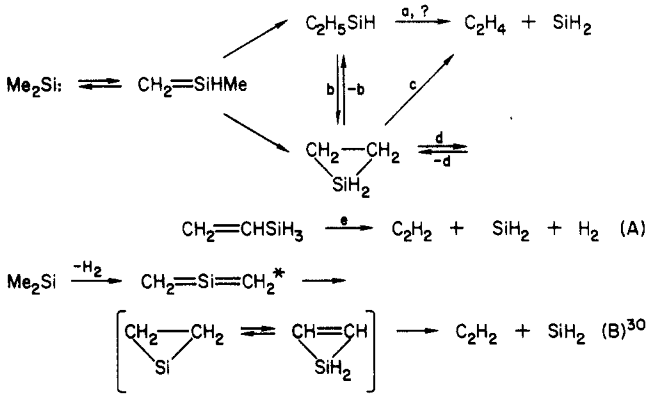


Figure 1. Comparative rate plots of dimethylsilane pyrolyses vs. cyclopropane: (A) static pyrolysis data, see ref 1; (B) 0.1% dimethylsilane, uninhibited; (C) 1.0% dimethylsilane, uninhibited; (D) 0.1% dimethylsilane, 3.0% toluene-d_8; (E) 0.1% dimethylsilane, 3.0% 1,3-butadiene. B–E in argon diluent.

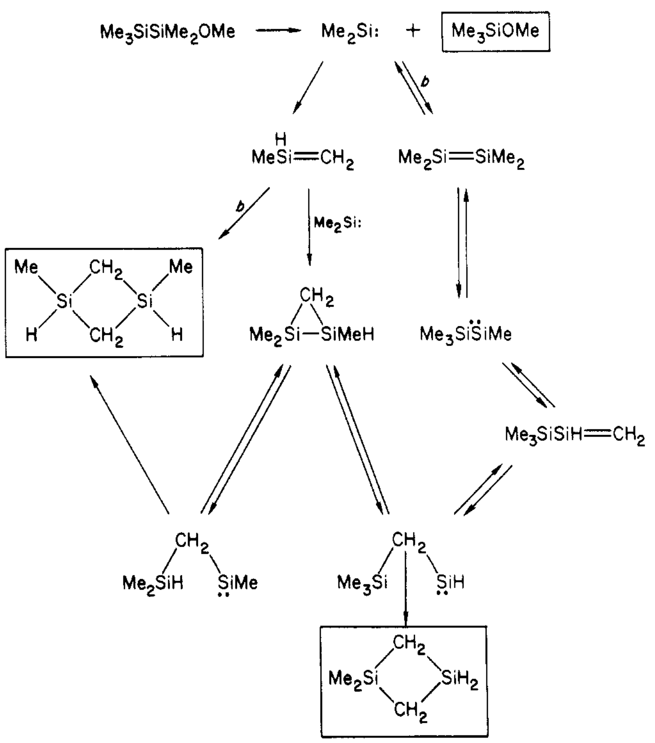
SCHEME II: Possible Mechanism for Ethylene Formation



positions. Disilenes are formed via silylene dimerization processes[3–6] and also via H_2 eliminations from disilanes. The latter are in turn produced from silylene Si–H insertions in the reactant. All these processes increase in importance with increasing reactant concentration.

The large yields of acetylene and ethylene must follow either directly or indirectly from reactions of dimethylsilylene. Dimethylsilylene is the most important intermediate in the reaction as it is produced in the major primary dissociation (reaction 1) as well as in free radical chains (e.g., Scheme I) and in various silylene chains (see later). The mechanisms by which ethylene and acetylene arise from dimethylsilylene are of special interest. Two reasonable pathways for ethylene production from dimethylsilylene are shown in Scheme IIA, where reaction e is not a direct process (see ref 4).

SCHEME III: Disilacyclobutane Formation from Me$_2$Si: [a]



[a] Major products are shown in brackets. [b] These are dimerization reactions.

The two pathways (a and b) are coupled by the isomerization between ethylsilylene and silacyclopropane, which recent results[29] indicate is relatively fast (i.e., rate b ≥ rate a, and rate −b ≥ rate d). Paths a and b are therefore operationally indistinguishable. Since ethylsilylene is produced in the initial step of the ethylsilane pyrolysis, product yields of the ethylsilane shock tube pyrolysis are directly applicable to the yields expected for the Me_2Si decomposition via Scheme II. These were mainly ethylene ($\phi_{C_2H_4} \simeq 0.90$) with quite small yields of vinylsilane ($\phi_{vs} \simeq 0.04$) and acetylene ($\phi_{C_2H_4} \simeq 0.05$), and acetylene yields increased at the expense of vinylsilane as temperatures were increased. This is all consistent with Scheme II and the known thermal stability of vinylsilane.[4] Since in the shock tube DMS pyrolysis acetylene is almost as important a product as ethylene, some other reaction channel besides Scheme IIA must be operative. We can only speculate on what this acetylene generating reaction channel might be. Vinylsilylene, via silacyclopropene, produces mainly acetylene at shock temperatures.[4] Therefore, it seems likely that silacyclopropene is a reaction intermediate. We propose the reaction sequence given in Scheme IIB. Acetylene yields increase rather strongly with increasing temperature, so the energy barrier to acetylene production must be significantly higher than the barrier to the formation of ethylene. The latter has a minimum value of 47 kcal/mol,[31] hence the activation energy to acetylene production from Me_2Si by the (C_2H_4/C_2H_2) yield variations must be greater than 55 kcal/mol.

Stirred Flow Studies: *Product Yields and Mechanistic Implications*. The product yield data of the stirred flow studies are shown in Table III. Mass loss was extensive. Less than 30% of the carbon was accounted for in the observed products. The major products were methane and ethylene with yields which increased with increasing temperature. Yields of the minor product, acetylene, also increased with increasing temperature. Methylsilane and trimethylsilane (important static system products) were observed but only in rather small yields; their yields decreased with increasing temperature.

In other flow studies involving generation of Me_2Si under similar conditions, significant yields of disilacyclobutane products have been observed.[14,15] The current mechanism for their production

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TABLE III: Product Yield Data from Stirred Flow Studies on DMS Pyrolysis[e]

T, K	% decompn	CH_4	C_2H_4	C_2H_2	C_3H_6	$MeSiH_3$	Me_3SiH	$C_2H_4 + C_3H_6$	system[a]
843	6.1	*b*	0.028	0.002	0.007	0.083	0.040	0.029	P
	7.1	*b*	0.051	0.004	0.012	0.060	0.105	0.063	P
	11.6	*b*	0.053	(0.030)[d]	0.016	0.068	0.087	0.069	P
890	12.6	0.157	0.068	*c*	0.030			0.098	K
	16.6	0.112	0.048	*c*				0.048	K
903	21.0	0.094	0.044	*c*				0.044	K
	21.5	*b*	0.122	*c*	0.018	0.105	0.072	0.140	P
	24.5	0.132	0.070	*c*	0.082			0.152	K
919	27.1	0.119	0.064	*c*	0.075			0.139	K
	38.5	0.233	0.137	*c*	0.103			0.240	K
	39.7	*b*	0.181	0.018	0.016	0.085	0.035	0.197	P
	41.4	*b*	0.169	0.015	0.014	0.080	0.036	0.183	P
942	42.2	0.203	0.117	*c*	0.089			0.206	K
	49.6	*b*	0.193	0.018	0.014	0.034	0.012	0.207	P
960	55.6	0.172	0.106	*c*	0.073			0.179	K
	57.1	0.164	0.100	*c*	0.066			0.166	K
	57.6	*b*	0.188	0.019	0.012	0.053	0.014	0.200	P
	63.3	*b*	0.176	0.018	0.011	0.043	0.010	0.187	P
	73.5	(0.411)[d]	0.221	*c*		0.055		0.221	K
980	74.8	0.310	0.205	*c*	0.071			0.276	K
	76.1	0.287	0.188	*c*	0.066			0.254	K
	79.2	0.285	0.148	*c*	0.053	0.043		0.201	K
992	79.6	0.271	0.155	*c*	0.052	0.019		0.207	K
	80.0		0.158	0.019	0.007	0.003	0.020	0.165	P
	80.5	*b*	0.150		0.007	0.018	0.002	0.157	P

[a] P: Studies of the products only. Products exiting the reactor were collected in a pumped on liquid N_2 trap, hence methane was not collected. The average pressure in the reactor for these runs was also rather low (~0.1 – 1.0-torr range). K: Studies of the kinetics of the DMS pyrolysis. Analyses were on direct aliquots of the gases exiting the reactor, and reaction pressures were about 6.8 torr. [b] No data. [c] Acetylene was observed in the kinetic runs but the amounts were too small to measure because of the gas aliquot size. Detection limits for integration of the chromatogram peaks were about 2%. [d] These are anamolously high values. [e] Yields = [Δ(product)/Δ(DMS)].

(proposed first by Barton)[16] has been modeled successfully by Davidson[17] and is shown in Scheme III. These reactions should be operative in our pyrolyses, and if so they will be important silylene sink reactions. While there was no evidence for disilacyclobutane products in our GLC chromatograms, we have recently found that these products do not elute well from our Poropak N columns. Therefore, they could have been (and probably were) among our products.

Mechanism of the Static System Pyrolysis of DMS. It has been very difficult to formulate a reasonable mechanism for the formation of methylsilane and trimethylsilane in the static system DMS pyrolysis. NS[1] hesitantly proposed free-radical processes at the walls (Scheme IV). However, besides the fact that these are very unusual wall processes, it is highly unlikely that free radicals are in any way involved in the static system pyrolyses of alkylsilanes (other than tetraalkylsilanes).

SCHEME IV: NS Free-Radical Mechanisms of DMS Static System Pyrolysis

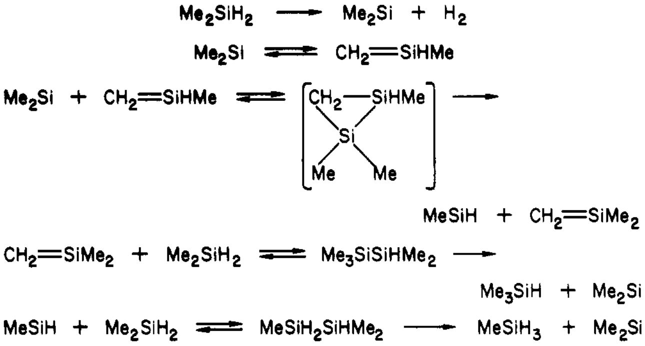
$$\mathrm{Me_2SiH_2} \xrightarrow{\text{wall}} \mathrm{Me_2\dot{S}iH + H\cdot}$$

$$\xrightarrow{\text{wall}} \mathrm{Me\dot{S}iH_2 + CH_3\cdot}$$

$$\mathrm{Me_2\dot{S}iH + Me_2SiH_2} \xrightarrow{\text{wall ?}} \mathrm{Me_3SiH + Me\dot{S}iH_2}$$

$$\mathrm{Me\dot{S}iH_2 + Me_2SiH_2 \rightarrow MeSiH_3 + Me_2\dot{S}iH}$$

SCHEME V: Previous Silylene Mechanism of DMS Static System Pyrolysis



To explain similar products in the methylsilane static system pyrolysis, we proposed an all silylene mechanism which applied to the DMS pyrolysis is as shown in Scheme V. Modeling of this scheme, however, revealed it to be much too slow at static and stirred flow temperatures to account for the $MeSiH_3$ and Me_3SiH yields observed.[32] Scheme VI, on the other hand, another all silylene mechanism, can account for the observations. This scheme mainly involves silylene insertions into reactant (Si–H) bonds and alkyl-substituted di- and trisilane decompositions—all very fast reactions even at low temperatures. The two key reactions are reactions 39 and 57. The 1,2-hydrogen elimination (reaction 39) is analogous to the rate-controlling reaction of the silane decomposition[18] (i.e., $Si_2H_6 \rightarrow Si_2H_4 + H_2$), and the disilene

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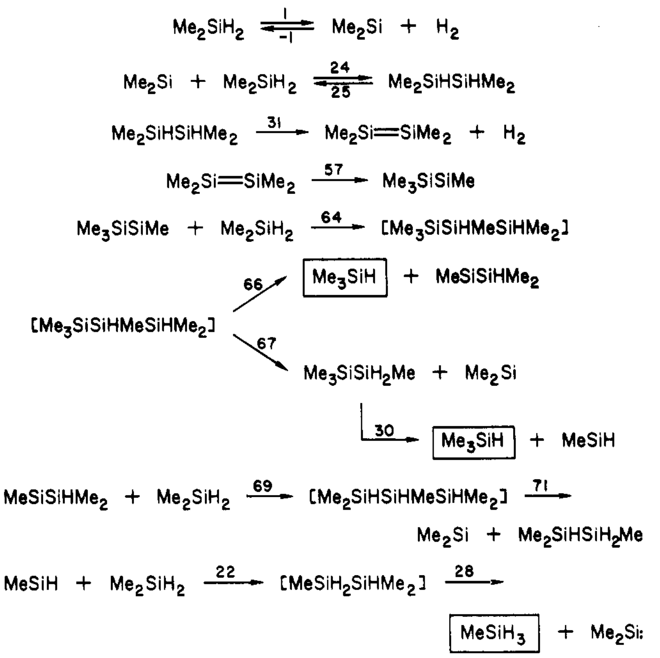
(26) The virtual absence of induced decomposition in the stirred flow studies is a surprising result (see Modeling). Also, the rather larger experimental errors for DMS when compared to the very small errors realized in the calibration studies on cyclopropane and cyclopentene strongly suggests reaction complexities for the DMS stirred flow reaction.

TABLE IV: Reactions in the Pyrolysis of Dimethylsilane[a,b]

	reactions	log *A*	*E*
1	A → DMS + $\mathrm{H_2}$	14.3	68.0
2	A → MS + $\mathrm{CH_4}$	14.8	73.0
3	A → R1 + $\mathrm{CH_3}$	17.0	87.0
4	A ← R1 + $\mathrm{CH_3}$	10.0	0.0
5	$\mathrm{CH_3}$ + A → R2 + $\mathrm{CH_4}$	9.9	11.4
6	$\mathrm{CH_3}$ + A → $\mathrm{MeH_2SiCH_2}$ + $\mathrm{CH_4}$	10.6	12.0
7	R1 + A → R2 + $\mathrm{MeSiH_3}$	9.9	14.4
8	R3 + A → R2 + $\mathrm{Me_3SiH}$	9.9	14.0
9	R1 → $\mathrm{CH_3}$ + S	15.6	64.0
10	R1 ← $\mathrm{CH_3}$ + S	10.0	0.0
11	R2 → $\mathrm{CH_3}$ + MS	15.9	63.5
12	R2 ← $\mathrm{CH_3}$ + MS	10.0	0.0
13	R3 → $\mathrm{CH_3}$ + DMS	16.1	62.6
14	R3 ← $\mathrm{CH_3}$ + DMS	10.0	0.0
15	$\mathrm{CH_3}$ + $\mathrm{CH_3}$ → $\mathrm{C_2H_6}$	10.2	0.0
16	$\mathrm{CH_3}$ + R2 → $\mathrm{Me_3SiH}$	10.2	0.0
17	$\mathrm{CH_3}$ + R3 → $\mathrm{Me_4Si}$	10.0	0.0
18	R2 + R1 → R2RDS	9.8	0.0
19	R2 + R2 → R2R2DS	9.5	0.0
20	S + A → R2DS	9.7	2.0
21	S + A ← R2DS	14.7	49.0
22	MS + A → R2RDS	9.8	2.0
23	MS + A ← R2RDS	14.5	49.0
24	DMS + A → R2R2DS	9.8	2.0
25	DMS + A ← R2R2DS	13.9	49.0
26	R2DS → DS20 + $\mathrm{H_2}$	14.3	54.4
27	R2DS → DMS + $\mathrm{SiH_4}$	13.0	49.0
28	R2RDS → $\mathrm{MeSiH_3}$ + DMS	13.2	49.0
29	R2RDS → DS21 + $\mathrm{H_2}$	14.4	54.4
30	R3RDS → $\mathrm{Me_3SiH}$ + MS	14.5	49.0
31	R2R2DS → DS22 + $\mathrm{H_2}$	13.7	54.4
32	$\mathrm{MeH_2SiCH_2\cdot}$ → MS + $\mathrm{CH_3}$	15.5	55.3
33	S + S → DS00	11.9	0.0
34	S + S ← DS00	15.3	58.0
35	S + MS → DS10	11.2	0.0
36	S + MS ← DS10	16.0	59.0
37	S + DMS → DS20	11.2	0.0
38	S + DMS ← DS20	16.2	60.0
39	MS + MS → DS11	11.0	0.0
40	MS + MS ← DS11	16.2	60.0
41	MS + DMS → DS21	11.2	0.0
42	MS + DMS ← DS21	16.2	60.0
43	DMS + DMS → DS22	11.0	0.0
44	DMS + DMS ← DS22	15.9	60.0
45	DS00 → $\mathrm{Si_2H_2}$ + $\mathrm{H_2}$	14.5	53.0
46	DS10 → MeSiSiH + $\mathrm{H_2}$	14.0	54.4
47	DS11 → MeSiSiMe + $\mathrm{H_2}$	14.2	55.0
48	DMS → $\mathrm{C_2H_4}$ + S	13.9	48.5
49	DMS → $\mathrm{VSiH_3}$	12.8	48.5
50	DMS → $\mathrm{C_2H_2}$ + $\mathrm{H_2}$ + $\mathrm{SiH_2}$	15.0	56.0
51	DMS → Si + $\mathrm{2CH_3}$	17.3	70.0
52	$\mathrm{VSiH_3}$ → VSiH + $\mathrm{H_2}$	15.1	63.3
53	$\mathrm{MeSiH_3}$ → MS + $\mathrm{H_2}$	15.0	50.6
54	$\mathrm{SiH_4}$ → S + $\mathrm{H_2}$	13.3	52.7
55	VSiH → $\mathrm{C_2H_2}$ + S	13.8	43.3
56	VSiH → $\mathrm{C_2H_4}$ + Si	15.0	50.6
57	DS22 → $\mathrm{Me_3Si\ddot{S}iMe}$	13.5	46.0
58	DS22 ← $\mathrm{Me_3Si\ddot{S}iMe}$	13.5	46.0
59	DS21 → $\mathrm{Me_2HSi\ddot{S}iMe}$	13.1	39.0
60	DS21 ← $\mathrm{Me_2HSi\ddot{S}iMe}$	13.1	39.0
61	DS20 → $\mathrm{Me_2SiHSiH}$	13.4	39.0
62	DS20 ← $\mathrm{Me_2SiHSiH}$	13.1	39.0
63	$\mathrm{Me_3Si\ddot{S}iMe}$ → carbosilanes	12.6	37.0
64	A + $\mathrm{Me_3Si\ddot{S}iMe}$ → R3RR2TS	9.8	2.0
65	A + $\mathrm{Me_3Si\ddot{S}iMe}$ ← R3RR2TS	13.6	49.0
66	R3RR2TS → $\mathrm{Me_3SiH}$ + $\mathrm{Me_2SiHSiMe}$	13.6	49.0
67	R3RR2TS → R3RDS + DMS	13.6	49.0
68	$\mathrm{Me_2SiH\ddot{S}iMe}$ → carbosilanes	12.4	37.0
69	A + $\mathrm{Me_2SiHSiMe}$ → R2RR2TS	9.8	2.0
70	A + $\mathrm{Me_2SiHSiMe}$ ← R2RR2TS	13.6	49.0
71	R2RR2TS → DMS + R2RDS	13.9	49.0
72	$\mathrm{Me_2SiH\ddot{S}iH}$ → carbosilanes	12.4	32.0
73	A + $\mathrm{Me_2SiHSiH}$ → R2R0R2TS	9.8	2.0
74	A + $\mathrm{Me_2SiHSiH}$ ← R2R0R2TS	13.9	49.0
75	R2R0R2TS → DMS + R2DS	13.9	49.0
76	DMS + $\mathrm{C_2H_4}$ → PROD1	8.5	2.0
77	MS + $\mathrm{C_2H_4}$ → PROD1	8.5	2.0
78	S + $\mathrm{C_2H_4}$ → PROD1	8.5	2.0
79	DMS + $\mathrm{C_2H_2}$ → PROD2	9.5	2.0
80	MS + $\mathrm{C_2H_2}$ → PROD2	9.5	2.0
81	S + $\mathrm{C_2H_2}$ → PROD2	9.5	2.0
	Added Sink Reactions for Stirred Flow Reactions		
82	DMS → wall	2.95	
83	MS → wall	2.95	
84	S → wall	2.95	
85	DS00 → PROD3	2.48	
86	DS10 → PROD3	2.48	
87	DS11 → PROD3	2.48	
88	DS20 → PROD3	2.48	
89	DS21 → PROD3	2.48	
90	DS22 → PROD3	2.48	

[a] A is $\mathrm{Me_2SiH_2}$, DMS in $\mathrm{Me_2Si}$, MS is MeSiH, S is $\mathrm{SiH_2}$. *Free radicals*: R1 is $\mathrm{MeSiH_2}$, R2 is $\mathrm{Me_2SiH}$, R3 is $\mathrm{Me_3Si}$. *Disilanes*: The number of methyl groups in each silicon center is indicated as R( )R( ) followed by DS. Thus $\mathrm{Me_2SiHSiHMe_2}$ is R2R2DS, and $\mathrm{Me_2SiHSiH_3}$ is R2DS. *Trisilanes*: The number of methyl groups at each silicon center is indicated as R( )R( )R( ) followed by TS. Thus $\mathrm{Me_2SiH_2SiHMeSiHMe_2}$ is R2RR2TS. *Disilenes*: A disilene is designated by DS followed by number indicating the number of methyls bonded to each silicon unit. Thus $\mathrm{Me_2Si{=}SiMe_2}$ is DS22 and $\mathrm{SiH_2{=}SiMeH}$ is DS10. *Carbosilanes*: Products following intramolecular insertion into C–H followed by the "Barton" isomerization reactions. [b] *Arrhenius parameter estimates*: (1) Arrhenius parameters of reaction 1 are those of NS[1] for the static system reaction under ethylene inhibition. These parameters may give rates which are too fast (see text). (2) Arrhenius parameters of reaction 2 were assigned to be consistent with the corresponding reaction in methylsilane and also to fit the methane yields of the stirred flow reaction. (3) All radical–radical recombination reactions involving $\mathrm{CH_3}$ were assigned $k = A = 10^{10.0}$ $\mathrm{M^{-1}\ s^{-1}}$. PROD 1 are ethylene trapping products; PROD 2 are acetylene trapping products; PROD 3 are wall polymerization products. (4) All radical–radical recombinations without $\mathrm{CH_3}$ were assigned $k = 10^{9.8}$ $\mathrm{M^{-1}\ s^{-1}}$. (5) Silylene insertions into Si–H bonds were assigned: *A* factors in the $10^{9.8}$–$10^{10.0}$ $\mathrm{M^{-1}\ s^{-1}}$ range and $E = 2.0$ kcal were assigned. (6) Bond fission reaction *A* factors were calculated from the assumed radical–radical recombination *A* factors and the estimated reaction entropies at 300 K.[19,20] No temperature corrections were made. Activation energies were equated to reaction enthalpies. (7) Disilane eliminations of $\mathrm{H_2}$ (reactions 26, 29, and 31) were calculated from the relation, $k_{\mathrm{H_2}} = \mathrm{rpd}(1,1) \times 10^{14.35} e^{-55300/RT} + \mathrm{rpd}(1,2) \times 10^{13.45} e^{-52900/RT}$ where rpd(1,1) and rpd(1,2) are the reaction path degeneracies for three-center (1,1) and four-center (1,2) eliminations, respectively. The resulting rate constant was then converted to Arrhenius form with $E = 54.4$ kcal/mol. The above relation is based on the observation of ref 21. (8) Disilane decompositions to monosilanes and trisilane decompositions to disilanes (reactions 21, 23, 25, 27, 28, 30, 65, 66, 67, 70, 71, 74, and 75) were all assumed to have activation energies of 49.0 kcal/mol. The *A* factors were calculated from the relations: $\mathrm{SiH_2}$ and MeSiH formation reactions, $A = \mathrm{rpd} \times 10^{14.2}$ $\mathrm{s^{-1}}$ when H migrates to a silicon center with alkyl substitution, and $A = \mathrm{rpd} \times 10^{13.6}$ when H migrates to an $\mathrm{SiH_3}$ silicon center; for reactions producing $\mathrm{Me_2Si}$, $A = \mathrm{rpd} \times 10^{13.0}$ when H migrates to an $\mathrm{SiH_3}$ silicon center, and $A = \mathrm{rpd} \times 10^{13.6}$ $\mathrm{s^{-1}}$ for H migration to a silicon with R group substitution. These rules reproduce all experimental rate constants for disilane pyrolyses at their average temperatures of study within about 30%.[22,23] (9) Silylene dimerizations to disilenes (reactions 33–44) and *disilene* eliminations of $\mathrm{H_2}$ (reactions 45–47) were assigned parameters from prior modeling studies (ref 3–6). (10) Vinylsilane and vinylsilylene decomposition kinetics (reactions 52, 55, and 56) are from ref 4. (11) Methylsilane and silane decomposition kinetics (reactions 53 and 54) are from ref 24 and 7, respectively. (12) Silylsilylene reactions to disilacyclobutane products (reactions 63, 68, and 72) were assigned parameters based on recent estimates from modeling studies of these reactions (I. M. T. Davidson, private communication). (13) Acetylene trapping reactions of silylenes (reactions 79–81) were assigned rate constants comparable to the corresponding Si–H insertion reactions. This is consistent with observed trapping rates.[25] (14) Ethylene trapping reactions of silylenes (reactions 76–78) were assigned rates 1/10 those of the acetylene trapping reactions. This is consistent with a former estimate.[12] (15) Gas-phase polymerization–depositions of silylenes (reactions 82–84) were assigned pseudo-first-order rate constants a factor of 3 higher than the corresponding constants for disilenes (reactions 85–90). The latter were assigned by analogy with reactions of the silane pyrolysis.[18] (16) Disilene to silylene isomerization involving methyl migration (reactions 57 and 58) were assigned parameters as in ref 15. Similar isomerizations involving H-atom migrations (reactions 59–62) were assumed to be faster with activation energies of about 39 kcal/mol. There are no data for these reactions. (17) Dimethylsilylene reaction channels (reactions 48–50) were assigned so as to be consistent with the reaction thermochemistries and to produce ethylene and acetylene in the approximate ratios observed.

SCHEME VI: Present All Silylene Mechanism of DMS Static System Pyrolysis[a]



[a] Reaction numberings correspond to the reactions of Table IV.

isomerization via methyl migration (reaction 57) is a critical step in the Barton mechanism (Scheme III). The validity of Scheme VI is evident from the modeling results for methyl- and trimethylsilane yields of the stirred flow and shock-induced reactions which follow. It is also quite successful in modeling the static system reaction, and this will be reported in a subsequent paper.

Modeling of the Dimethylsilane Pyrolysis

The Shock Tube Reaction. Besides the three primary dissociation reactions, H_2 elimination (reaction 1), CH_4 elimination (reaction 2), and (Si–C) bond rupture (reaction 3), the kinds of reactions which reasonably should be involved in the DMS pyrolysis (by analogy with other alkylsilane pyrolyses and from the earlier discussions) are silylene insertions into Si–H bonds (of DMS and other substrates), decompositions of the resulting disilanes (or trisilanes) via 1,2-H shifts (to silanes and silylenes) and H_2 eliminations (to disilenes), silylene dimerizations to disilenes and the disilene reverse decompositions, disilene H_2 eliminations and isomerizations (to silylenes), free-radical recombinations, free-radical H abstractions (from DMS), free radical decompositions, and finally dimethylsilylene reactions to ethylene, vinylsilane, and acetylene (as in Scheme II). Acetylene and ethylene trapping reactions of silylenes[12] are also possible for pyrolyses carried to high conversions. A comprehensive list of reactions of the above types relevant to the DMS pyrolysis are given in Table IV. These comprise our proposed mechanism. The parameters assigned to the various reactions come from literature values for the same or analogous reactions, or in the absence of data, have been estimated by assumptions and considerations detailed in the footnotes to Table IV.

TABLE V: Modeling Results for DMS Pyrolysis in the Shock Tube Reaction[a]

	0.10% DMS, 1200 K			0.10% DMS, 1280 K		
product	exptl	set A	set B	exptl	set A	set B
CH_4	0.48	0.357	0.293	0.44	0.366	0.320
C_2H_6	0.17	0.049	0.017	0.14	0.150	0.071
C_2H_4	0.34	0.209	0.282	0.33	0.197	0.286
C_2H_2	0.19	0.115	0.155	0.24	0.133	0.193
$MeSiH_3$		0.057	0.053		0.020	0.021
Me_3SiH		0.008	0.034		0.013	0.006
H_2	1.00	0.727	0.845	1.12	0.873	1.01
% decompn[b]	15.3	6.79	5.91	54.6	34.2	31.9

	1.0% DMS, 1200 K			1.0% DMS, 1280 K		
product	exptl	set A	set B	exptl	set A	set B
CH_4	0.46	0.326	0.280	0.47	0.386	0.328
C_2H_6	0.036	0.020	0.007	0.028	0.085	0.032
C_2H_4	0.18	0.128	0.147	0.22	0.168	0.205
C_2H_2	0.085	0.071	0.082	0.13	0.114	0.138
$MeSiH_3$	0.036	0.097	0.088	0.02	0.030	0.031
Me_3SiH	0.047	0.039	0.029	0.05	0.037	0.017
H_2		0.567	0.619	1.12	0.849	0.889
% decompn[b]	7.1	16.6	11.7	40.5	59.2	48.9

[a] Set A: Reaction 51 included along with reactions 1–81 (Table IV). Set B: Reaction 51 is excluded from reactions 1–81 (Table IV). [b] % decomposition is for a residence time of 300 μs.

TABLE VI: Modeling Results for the DMS Pyrolysis in the Stirred Flow Reactor

	product yields					
	CH_4	C_2H_4	C_2H_2	$MeSiH_3$	Me_3SiH	% reaction[c]
T = 860 K						
exptl	0.10	0.03	0.003	0.08	0.08	5.1
set A[a]	0.007	0.014	0.003	0.009	0.27	93.9
adjusted[b]	0.13	0.02	0.004	0.02	0.03	7.47
T = 910 K						
exptl	0.11	0.05	0.01	0.07	0.07	20.8
adjusted[b]	0.15	0.07	0.02	0.006	0.05	41.3
T = 960 K						
exptl	0.16	0.11	0.02	0.05	0.03	56.3
adjusted[b]	0.20	0.14	0.04		0.03	83.5

[a] Modeling results using reactions 1–81 (Table IV). [b] Modeling results including gas-phase polymerization and deposition reactions represented by pseudo-first-order reactions 82–90 (Table IV). [c] The "experimental" conversion was calculated from the experimental Arrhenius parameters of NS and reaction times of 40 s at 860 K, 20 s at 910 K, and 10 s at 960 K. These produce slightly higher values than were observed at the higher temperatures. Experimental yields were obtained from smoothed curves of the product yield data of Table III.

Modeling results at 1200 and 1280 K for the mixtures containing no trapping agents (mixtures B and C) are shown in Table V. Two sets of results are shown: set A and set B. The set A results were obtained with reactions 1–81 of Table IV with the parameters indicated. It includes, via reaction 51, an additional methyl radical source in the DMS chain. The rather high CH_4 and C_2H_6 yields observed seem to require some such reaction, although it need not be reaction 51; any other chain intermediate source would serve equally well. The set B results were obtained without reaction 51, and while the CH_4 and C_2H_6 yields are clearly too low, somewhat better agreements in the silylene chain product yields (i.e., C_2H_4 and C_2H_2) are realized by this set.

The factor of two or better agreement in percent decomposition for both sets, except at 1200 K for the 0.10% DMS mixture, shows that most of the induced decomposition observed is reasonably well explained by the mechanism. Not explained, however, are the decreasing conversions with increasing DMS concentrations. Our modeling predictions are the reverse and we cannot explain the discrepancy.

While the modeling results are far from perfect, considering the obvious reaction complexity, we feel gratified with the results.

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(27) Molecular methane elimination contributes about 9% to the primary process reactions of methylsilane at shock temperatures.[3] On the basis of reaction path degeneracy alone, a somewhat higher contribution is expected in the DMS pyrolysis.

(28) Reaction numbering corresponds to the mechanism of Table III.

(29) Results on *n*-$BuSiH_3$ decomposition and silylene trapping by ethylene, to be submitted for publication.

(30) Because of silicon's d orbitals, this species need not be linear. Hence its formation via a five-center transition state from dimethylsilylene is neither energetically nor sterically unreasonable. This species has been proposed as an intermediate in the decomposition of spirosilicon compounds.[13]

(31) $\overline{\Delta H^\circ}_f(Me_2Si:) \simeq 24.5 \pm 3$ kcal/mol, $\overline{\Delta H^\circ}_f(SiH_2) = 59.0$ kcal/mol, $\overline{\Delta H^\circ}_f(C_2H_4) = 12.5$ kcal/mol, hence for the reaction $Me_2Si \rightleftarrows C_2H_4 + SiH_2$ we have $\Delta H^\circ \simeq 47 \pm 3$ kcal/mol.

(32) To be important, the dimethylsilylene metathesis reaction must be fast. This is only marginally true under shock tube reaction conditions.

In general, all the products observed are predicted and at close to the proper yield levels. Temperature and concentration effects are also in most cases predicted properly as well as silylene and free-radical chain-induced levels of decomposition. It appears, therefore, that most of the reactions of importance for the dimethylsilane shock tube pyrolysis are contained in the Table IV mechanism.

The Stirred Flow Reaction. A straightforward application of the mechanism and rate constants (1–81) of Table IV produces the "base set" results shown in Table VI (see $T = 860$ K). The predicted product yields (other than CH_4) are in fair agreement with those observed but the percent reaction predictions are much too high. Thus the modeling predicts extensive chain-induced reaction in the stirred flow system which is not observed. Clearly, some very efficient sink reactions for the intermediates must be operative under stirred flow reaction conditions. In our successful modeling fits of the silane pyrolysis[18] we proposed gas-phase disilene polymerization–deposition processes as major sink reactions. We also found, by modeling the polymerizations, that their rates could be represented reasonably well by simple pseudo-first-order reactions at the walls with rate constants in the $k_w \simeq 300\ s^{-1}$ range. Assuming that similar polymerization–deposition reactions apply to the silylenes and disilenes of the DMS system (i.e., adding reactions 82–90, Table IV) produces the results shown under "adjusted set" in Table VI. All yield predictions are now in fairly good agreement with the data (including CH_4), and the conversion predictions are much closer, although still too high by 60–80%. Increasing the sink reaction rate constants to their upper limits (i.e., increases by factors of 10–100) does not significantly effect conversion limits. This is understandable since a significant fraction of the intermediates produced in the primary dissociation reactions (i.e., Me_2Si, MeSiH, $CH_3\cdot$) necessarily react with DMS before they can be scavenged (even with very fast sink reactions) and this must lead to rates close to factors of two faster than the primary process dissociation rates. Therefore, either our stirred flow reaction rates are in error (i.e., too low) or the Arrhenius parameters of NS[1] do not apply directly to the primary dissociation reactions of DMS. We are presently restudying the static system pyrolysis to see if we can resolve this problem. In other respects the modeling is again gratifying as product predictions and yields are generally in good agreement with the data. The single exception is propylene whose formation cannot be explained by any reasonable gas-phase reaction channel presently known to us.

Conclusions

We have shown that the shock-induced pyrolysis of dimethylsilane is a complex process involving both free-radical and silylene chains. The latter cannot be completely quenched by additions of trapping agents. At high temperatures dimethylsilylene decomposes to ethylene, through the intermediacy of a silirane, and to acetylene. The latter reaction channel may involve the intermediacy of silacyclopropene.

Stirred flow and static system pyrolyses are dominated by silylene chains, and reaction intermediate sink reactions are proposed to be disilene and silylene polymerization–deposition processes.

The main primary dissociation reactions of DMS are H_2 and molecular methane elimination. Present data cannot establish the ratio of the 1,1- and 1,2-hydrogen elimination channels, but by analogy with the methylsilane reaction it is reasonable to believe that both eliminations occur. Since our modeling of the methane yields of the stirred flow system agree well with the data (methane produced here arises mainly from primary processes) the reaction 2 parameters for molecular methane eliminations are probably fairly reliable. On this basis, methane elimination accounts for about 17% of the total primary process dissociation at stirred flow temperature and for about 19% at shock tube temperatures. The Arrhenius parameters for CH_4 elimination establish an activation energy of 24.5 kcal/mol (based on the pressure standard state) for methylsilylene insertion into the C–H bond of methane. Since E_{act} for silylene insertion into methane is about 19.0 kcal/mol,[3] it appears that increased alkyl substitution at the silicon center in silylenes raises the activation energy for insertion into (C–H) bonds by about 5 kcal/CH_3. Finally, the DMS pyrolysis, in spite of its complexity, can be reasonably modeled with regard to products and conversions at essentially all reaction temperatures of interest by employing the mechanism of Table IV.

Acknowledgment. The authors are indebted to the Air Force for support of this research via AFOSR (83-0209).

Registry No. DMS, 1111-74-6; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_2, 74-86-2; C_3H_6, 115-07-1; $MeSiH_3$, 992-94-9; Me_3SiH, 993-07-7.

Single-Pulse Shock Tube Study on the Stability of Perfluorobromomethane

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Perfluorobromomethane has been decomposed in comparative rate single-pulse shock tube experiments. Reaction extent was determined by measuring the ethylene yields from the induced decomposition of cyclopentane. The important processes are $CF_3Br \rightarrow CF_3\cdot + Br\cdot$, CF_3/Br + cyclopentane → cyclopentyl → CF_3H/HBr, and cyclopentyl → allyl + C_2H_4. Under our reaction conditions (950–1100 K and 2.5–8 atm), the unimolecular decomposition processes are clearly in the falloff region with k/k_∞ in the 0.25 to 0.6 range. The pressure dependence is of the order of $p^{(0.38\pm0.05)}$. RRKM calculations that fit the results yield $k_\infty(CF_3Br \rightarrow CF_3\cdot + Br\cdot) = 10^{14.95} \exp(-34290/T)\ s^{-1}$ and a step size down of 5.6 ± 1.4 kJ, with argon as collision partner. Failure to observe any effects with cyclopentane concentrations as high as 5% permits an upper limit to be set on the efficiency of a large polyatomic as collision partner. The high-pressure rate expression is consistent with a heat of formation ($\Delta H_f(CF_3) = -460.3\ kJ\ mol^{-1}$) which we derived independently from considering the equilibrium for the reaction $CF_3 + CH_4 \rightarrow CH_3\cdot + CF_3H$. This leads to a rate of combination between $CF_3\cdot$ and $Br\cdot$ of $10^{10.3}\ L\ mol^{-1}\ s^{-1}$.

Introduction

This paper is concerned with the breaking of the C–Br bond in CF_3Br. Experiments are carried out in a single-pulse shock tube in the presence of cyclopentane as a free radical scavenger and with an internal standard. The role of cyclopentane is to react with the CF_3 and Br radicals that are formed as a result of bond breaking. The sequence of reactions is then

$$CF_3\cdot/Br\cdot + \text{cyclopentane} \rightarrow \text{cyclopentyl} + CF_3H/HBr$$

$$\text{cyclopentyl} \rightarrow \text{allyl} + C_2H_4$$

$$\rightarrow \text{cyclopentene} + H\cdot$$

$$H + \text{cyclopentane} \rightarrow \text{cyclopentyl} + H_2$$

Thus every reactive radical that is formed in the system leads

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