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# A Kinetic Study of the Reaction of Methylene Radicals with Dimethylsilane.

# The Decomposition of Chemically Activated Trimethylsilane

# and Methylethylsilane<sup>1a</sup>

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A study of the decomposition of chemically activated trimethylsilane and methylethylsilane is reported. Chemical activation was by the insertion of singlet methylene, from the photolysis of diazomethane at 3660 Å and 24°, into the C-H and Si-H bonds of dimethylsilane. The total rate constants for trimethylsilane,  $k_{\rm MES}$ , and methylethylsilane,  $k_{\rm MES}$ , unimolecular decomposition were found to be 2.93  $\times$  10<sup>7</sup> sec<sup>-1</sup> and 3.30  $\times$  10<sup>7</sup> sec<sup>-1</sup>, respectively. H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> were formed as decomposition products in the presence of the radical scavengers, oxygen and 1,3-butadiene, indicating they are formed by molecular elimination processes. The experimental results combined with RRKM calculations infer that Si-C bond rupture and methane elimination are the major primary decomposition paths for chemically activated trimethylsilane, and Si-C bond rupture and molecular hydrogen elimination are the major primary decomposition paths for chemically activated methylethylsilane. The rate constant for methyl rupture from the chemically activated trimethylsilane, 2.2 ± 0.8  $\times$  10<sup>7</sup> sec<sup>-1</sup>, yields an A factor for Si-C bond rupture in trimethylsilane, *via* RRKM theoretical calculations, equal to 10<sup>16,6</sup> ± <sup>0.6</sup> sec<sup>-1</sup>.

# Introduction

Although alkanes thermally decompose by unimolecular C-C bond fissions,<sup>2</sup> recent pyrolysis studies suggest that some silanes and alkylsilanes decompose at least in part by direct molecular elimination.<sup>3-10</sup> It has been pointed out<sup>11,12</sup> that a fine balance exists between the radical and molecular elimination modes of decomposition in silicon compounds, and care must be taken in evaluating the relative importance of the two paths for different silicon compounds. For example, it has been proposed that the pyrolysis of  $Si_2H_6^{3a,5-8}$  yields  $SiH_2$ and SiH<sub>4</sub> as the primary decomposition products, but (CH<sub>3</sub>)<sub>3</sub>SiH<sup>13</sup> appears to decompose by Si-H and Si-C bond rupture at 1000°K. Both decomposition modes are operative during the pyrolysis of CH<sub>3</sub>SiH<sub>3</sub>,<sup>3b,4b,12</sup> where H<sub>2</sub> molecular elimination and Si-C bond rupture seem to occur with comparable importance.

Pyrolysis studies suffer frequently from heterogeneous effects and complicating secondary reactions, which lead to complex chain mechanisms, and obscure the

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primary rates. Considerable effort has been spent in determining the Arrhenius parameters for the initiation reactions of alkane decompositions, but there is still a major question as to the order of magnitude of the A factors for C–C bond rupture.<sup>2,14</sup> Using a chemical activation technique<sup>15</sup> one can minimize the problems that plague thermal studies, and a comparison of the data for the two types of studies is of interest.

In this paper we present the results of a low-pressure study of diazomethane-dimethylsilane photolyses at 3660 Å. An internal standard, tetramethylsilane, was used to determine the unimolecular decomposition rate constants for the chemically activated trimethylsilane and methylethylsilane. Product analyses, with and without radical scavengers added to the reaction mixtures, were used to establish the probable decomposition paths of the energized trimethylsilane and methylethylsilane. We reported the high pressure results for this system previously.<sup>16a</sup>

## **Experimental Section**

Apparatus and Materials. All gas handling was performed with standard high vacuum equipment. A Toepler pump was used to transfer noncondensables. The volume used to measure out the reactants was isolated by greaseless valves. In all other phases of the gas handling process the pressures were low enough to ensure that no measurable absorption in stopcock grease with subsequent contamination occurred. The source of photolysis radiation was a Hanovia 673A medium-pressure mercury arc lamp. The 3660 Å line was isolated either by Hanovia filter 16223B or Esco Products No. 5860 filter. The photolyses were carried out in seasoned Pyrex vessels, varying in volume from 1 to 12,710 cm<sup>3</sup>. An Aerograph 90-P3 gas chromatograph and a Hitachi, Model RMU-6E, mass spectrometer were used for product analyses.

Baker lecture bottle 1,3-butadiene (99.5% pure) contained no interfering impurities and was used without further purification. The remaining materials used in this study were the same as those described previously.<sup>16</sup>

Procedure. Dimethylsilane-diazomethane and dimethylsilane-tetramethylsilane-diazomethane mixtures with and without added oxygen or 1,3-butadiene were photolyzed from 2 to 20 hr depending on the total pressure. All of the photolyses were performed at room temperature ( $\sim 24^{\circ}$ ). No surface effects were observed by varying reactor volumes for experiments at the same pressure.

A slow dark reaction occurred between dimethylsilane and oxygen to produce hydrogen and methane. No other products of interest were formed from the dark reaction. The dark reaction was slow enough, less than 1% of the dimethylsilane was destroyed during 24 hr, to ensure that the alkylsilane products of interest were not destroyed by the oxygen. In all experiments oxygen was removed upon completion of the photolysis. There was no ethane or propane formed from photolysis of diazomethane in the presence of only oxygen or 1,3-butadiene. The measurable products were hydrogen, ethylene, acetylene, and propylene. Products formed from methylene + 1,3-butadiene were not measured. A correction for the small amount of methane formed by the photolysis of diazomethane and 1,3-butadiene mixtures was applied to the dimethylsilanediazomethane-1,3-butadiene photolyses at each pressure. The maximum correction was 15%.

Analysis. Upon completion of the photolyses, a sample of an argon-neohexane calibration mixture was added to the photolyzed reaction mixture. The noncondensables (H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar) at  $-196^{\circ}$  were removed by means of a Toepler pump. The condensable components were trapped in a U-tube at  $-196^{\circ}$ . H<sub>2</sub> and  $CH_4$  were analyzed on the mass spectrometer and measured relative to Ar. The condensable components were analyzed by glpc and measured relative to neohexane. The glpc column was packed with 25 ft 30%dibutyl phthalate on Chromasorb and operated at room temperature. A known mixture of H<sub>2</sub>, CH<sub>4</sub>, and Ar was run on the mass spectrometer after each  $H_2$  and CH<sub>4</sub> analysis in order to quantitatively calibrate the mass spectrometer for H<sub>2</sub>, CH<sub>4</sub>, and Ar. Mixtures similar to the reaction mixtures were used to calibrate the glpc column for the measured products.

Since ethane and ethylene had the same retention time on the DBP column, the ethane analyses were performed by trapping the ethane and ethylene peak and the neohexane peak as they eluted from the DBP column and then analyzing this trapped portion on a 30-ft AgNO<sub>3</sub>-butanediol (sol.) + 25-ft dinonyl phthalate column.

## **Results and Interpretation of the Data**

*Products.* The major condensable products of the reaction system were trimethylsilane (TMS) and methylethylsilane (MES). When tetramethylsilane (TEMS) was added to the reaction mixtures, ethyltrimethylsilane (ETMS) was a major product. In the

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Figure 1. Plot of TMS/MES vs. 1/P (cm<sup>-1</sup>) for CH<sub>2</sub>N<sub>2</sub>-DMS photolyses at 3660 Å: , no scavenger added; O, oxygen added. The collision frequency, w, is equal to  $2.09 \times 10^8 \text{ sec}^{-1}$ cm<sup>-1</sup> for points with no scavenger added, 2.12  $\times$  108  $\sec^{-1}$  cm<sup>-1</sup> for points with 1,3-butadiene added, and  $2.05 \times 10^8 \text{ sec}^{-1} \text{ cm}^{-1}$  for points with oxygen added. These w's were calculated using the following collision diameters: TEMS, 8.6 Å; TMS, 7.2 Å; MES, 7.2 Å; DMS, 6.6 Å; DM, 5.5 Å; Bd, 6.6 Å; and O<sub>2</sub>, 3.6 Å. These values are the Lennard-Jones collision diameters multiplied by the square root of the collision integral  $\Omega^{2,2*}(kT/\epsilon)(S. C. Chan,$ B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, J. Phys. Chem., 74, 3169 (1970)). The collision diameters for the alkylsilanes were determined by assuming that a Si atom contributes as much to the collision diameter of a molecule as two carbon atoms in an alkane. The deactivation efficiency of oxygen was taken as 0.25 in accordance with the results of G. H. Kohlmaier and B. S. Rabinovitch, J. Chem. Phys., 38, 1709 (1963).

absence of any radical scavenger  $H_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and ethyldimethylsilane (EDMS) were also formed. Upon addition of  $O_2$  or 1,3-butadiene (Bd) to the reaction mixtures the formation of  $C_3H_8$  and EDMS was completely suppressed. The presence of either  $O_2$  or Bd should eliminate radical recombination reactions since  $O_2$  scavenges ground triplet state methylenes<sup>17</sup> as well as other triplet or doublet radicals<sup>18</sup> which are formed in the system. H-atom, alkyl radical and triplet methylene additions to 1,3-butadiene are fast.<sup>19</sup> No attempt was made to measure ethylene, acetylene, and propylene, which are formed by pure diazomethane photolyses.

DMS-DM. In Figure 1 the ratios of TMS/MES vs. 1/P are given for DMS-DM photolyses at 3660 Å in the presence and absence of O<sub>2</sub>. For 1/P from 2 to 22 cm<sup>-1</sup> there appears to be no detectable difference between the two sets of points. But an average of the high pressure points, 1/P < 2, gives a value for TMS/MES = 2.30 in the presence of O<sub>2</sub> and 2.69 in the absence of any scavenger.

Propane and ethyldimethylsilane (EDMS) formation were completely suppressed upon addition of  $O_2$  or 1,3butadiene to the reaction mixtures, indicating they probably are formed by radical recombination processes. The high pressure ratios of EDMS/MES and  $C_{2}H_{3}/MES$  in the absence of a scavenger were 0.24 and 0.03, respectively. The formation of  $C_{\vartheta}H_{\vartheta}$  and EDMS indicate that ethyl radicals are produced in this reaction system.

product ratios, H<sub>2</sub>/MES, CH<sub>4</sub>/TMS, and The C<sub>2</sub>H<sub>6</sub>/TMS, are presented in Table I. It was found that H<sub>2</sub> was formed from photolyses of pure CH<sub>2</sub>N<sub>2</sub>. The H<sub>2</sub> possibly is formed by molecular elimination from chemically activated  $C_2H_4$ , formed by methylene recombination or the reaction of methylene with diazomethane.20 The addition of 1,3-butadiene did not eliminate H<sub>2</sub> formation. It was found that this source of  $H_2$  could be minimized by decreasing the fraction of  $CH_2N_2$  in the reaction mixtures with DMS. A ratio of DMS/DM equal to 8.5 gave no  $H_2$  at a relatively high pressure of 14.7 cm and ratios of DMS/DM in the range of 10–20 gave a linear relationship for  $H_2/MES$  vs. 1/P(Figure 2). These results indicate that the  $H_2$  formation from  $CH_2N_2$  photolyses is eliminated by using a ratio of DMS/DM  $\simeq$  10–20.

The data in Table I and Figure 3 show that within experimental error the  $CH_4/TMS$  ratios are invariant upon addition of Bd to the reaction mixtures, indicating that  $CH_4$  probably is formed entirely by a molecular elimination process. It should be noted that at the higher pressures  $CH_4$  formation in the absence of a scavenger is negligible.

The  $C_2H_6/TMS$  ratios in Table I are greatly reduced when Bd or  $O_2$  is added to the system, but  $C_2H_6$  forma-



Figure 2. Plot of  $H_2/MES$  vs. 1/P (cm<sup>-1</sup>) for  $CH_2N_2$ -DMS photolyses at 3660 Å:  $\Box$ , DMS/CH<sub>2</sub>N<sub>2</sub> = 5; O, DMS/CH<sub>2</sub>N<sub>2</sub> = 10-20. The line was determined by the method of least-squares with the intercept forced to zero.

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The Journal of Physical Chemistry, Vol. 76, No. 4, 1972

Total pressure <sup>a</sup>	Bd/DMS	% O2	(Bd + DMS)/DM	TMS/MES	H <sub>2</sub> /MES	CH4/TMS	C <sub>2</sub> H <sub>6</sub> /TMS
14.69	0.00	0	8.5		0,00		
3,41	0,00	0	23.4	2.60	0,10	0.09	
2.90	0.00	0	5,1	2.85			0.19
2.35	1.90	0	5.8			0.04	0.03
0.374	0.00	0	5.1	2.53			0.40
0.360	0,00	17	3,6	2.58			0,03
0.281	3.25	0	5.6			0.22	0.07
0.239	0.00	0	5.5	2.66	0.91	0.36	
0.212	0,00	0	18.8		0.68	0.34	
0.165	0.00	16	3.4	2,23			0.05
0.152	0.00	0	19.6	2.36	0.52	0.36	
0.132	3,11	0	5.5			0.33	0.16
0.127	0.00	0	4.0	2.40			0.54
0.100	0.00	0	8.3		0.66	0.31	
0.104	0,00	22	3.6	2.64			0.09
0.0989	3.80	0	10.0				0.08
0.0977	0.00	0	9.0	2.37	0,65	0.37	
0,0973	3,22	0	8.1			0.32	
0.0956	2.95	0	4.4			0.47	0.15
0.0869	0.00	0	16.4	2.12	0.87	0,52	
0.0767	2.44	0	2.7			0,58	
0.0764	0,00	11	2,8	2.28			0.08
0.0745	1.91	0	2.8			0.42	0,09
0,0725	0.00	0	6.6	2.26	1.64	0.68	
0.0648	4,60	0	5.6				0.20
0.0645	0.00	0	6.2	2,25	1.45	0.71	
0,0614	3,36	0	3.2			0.52	0.14
0.0612	1,05	0	5.2				0.24
0.0569	0.00	0	3.9	2.30			0.77
0,0520	0.00	0	11.3	1.94	1.20	0.76	
0.0507	0,00	20	3.1	2,40			0.12
0.0472	2.52	0	2.7			0.70	0.34
0.0465	3.11	0	3.7				0.26
0.0464	0,00	18	3.5	2.53			0.16
0.0451	5,19	0	3,6				0.44
0.0427	3.12	0	6.1			0.92	0,15
0.0404	1,00	0	7.4			0.78	
0.0357	2.08	0	2,6			1.09	
0.0352	2.87	0	2.8			0.99	
cm1		-					

Table I: Product Ratios from Photolysis of Diazomethane-Dimethylsilane Mixtures of 3660 Å

<sup>a</sup> The pressures are expressed in cm.



Figure 3. Plot of CH<sub>4</sub>/TMS vs.  $1/P \text{ (cm}^{-1})$  for DMS-CH<sub>2</sub>N<sub>2</sub> photolyses at 3660 Å:  $\Box$ , no scavenger added; O, Bd added. The line through the CH<sub>4</sub>/TMS points with Bd added was determined by the method of least squares with the intercept forced to zero. The dashed line is the CH<sub>4</sub>/TMS plot that would result if  $k_{24} = 0.36 \times 10^7 \text{ sec}^{-1}$ .

The Journal of Physical Chemistry, Vol. 76, No. 4, 1972

tion is not completely suppressed. The  $C_2H_6/TMS$  ratios with  $O_2$  as a scavenger were more reproducible than the ratios with Bd as a scavenger; however, the agreement is satisfactory and the data reveal that  $C_2H_6$  probably is formed in part by a molecular elimination process. The MES peak was not measured in the experiments with Bd added, since Bd and MES had identical glpc retention times.

TEMS-DMS-DM. The ETMS/TMS ratios for the photolysis of tetramethylsilane-dimethylsilanediazomethane mixtures at 3660 Å with and without  $O_2$ added are presented in Table II. MES was not measured in this system since in the glpc analyses the tail of the large tetramethylsilane peak swamped the MES peak. The high pressure ETMS/TMS ratio is increased upon  $O_2$  addition. At the lower pressures the difference between the ratios in the presence and absence of  $O_2$  is less significant. Also, the ETMS/TMS

Total	(DMS + TEMS)/	Ø7 <b>()</b> .	TTMS/TMS	
pressure	$CH_2N_2$	$\gamma_0  \mathbf{U}_2$	EINIO/INIO	
67.8	6.8	0	0.86	
19.3	10.4	0	0.98	
12.2	6.2	0	1.16	
10.4	11.4	0	0.61	
4.48	7.6	0	1.08	
1.05	7.9	0	1.32	
0.231	7.6	0	1.85	
129.0	7.9	31	1,26	
117.2	6.1	<b>48</b>	1.17	
99.9	7.2	18	1.06	
19.6	6.3	30	1,30	
19.1	8.2	10	1.23	
9.01	6.5	12	1.16	
8.13	5.8	30	1.34	
4.72	6.5	11	1.33	
1.87	6.4	<b>28</b>	1.62	
1.04	6.2	<b>27</b>	1.41	
0.479	6.7	<b>28</b>	1.74	
0.379	6.6	12	1.97	
0.290	6.3	<b>27</b>	2.16	
0.258	7.6	10	<b>2</b> , $04$	
0.144	6.0	<b>34</b>	2.81	
0.143	6.1	13	2.67	
0.116	6.3	27	2.84	
0.093	4.9	27	3.72	
<sup>a</sup> All pressures are expressed in cm.				

Table II: ETMS/TMS Product Ratios

ratios are independent of the percent  $O_2$  added to the reaction mixture in the range of 10-50%.

#### Discussion

1

*Mechanism.* The following reaction scheme, which is consistent with previous work,<sup>16,21</sup> satisfactorily explains the observed products and their variations in the present system.

$$CH_2N_2 \xrightarrow{3660 \text{ \AA}} {}^1CH_2 + N_2$$
 (1a)

$$CH_2N_2 \xrightarrow{3660 A} {}^{3}CH_2 + N_2$$
 (1b)

$$CH_2 + (CH_3)_2 SiH_2 \longrightarrow (CH_3)_3 SiH^*$$
(2)

$$\rightarrow$$
 C<sub>2</sub>H<sub>5</sub>(CH<sub>3</sub>)SiH<sub>2</sub>\* (3)

$$CH_2 + (CH_3)_4Si \longrightarrow C_2H_5Si(CH_3)_3^*$$
 (4)

$$^{1}\mathrm{CH}_{2} + \mathrm{M} \longrightarrow ^{3}\mathrm{CH}_{2} + \mathrm{M}$$
 (5)

$$CH_2 + (CH_3)_2 SiH_2 \longrightarrow CH_3 + (CH_3)_2 SiH \quad (6)$$

$$CH_3 + CH_2N_2 \longrightarrow C_2H_5 + N_2 \tag{7}$$

$$CH_{3} + (CH_{3})_{2}SiH \longrightarrow (CH_{3})_{3}SiH$$
(8)

$$C_2H_5 + (CH_3)_2SiH \longrightarrow C_2H_5(CH_3)_2SiH$$
 (9)

$$C_2H_5 + CH_3 \longrightarrow C_3H_8 \tag{10}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6$$
 (11)

$$(CH_{\vartheta})_{\vartheta}SiH^* \xrightarrow{\kappa_{TMS}} products$$
 (12)

$$\xrightarrow{w}$$
 (CH<sub>3</sub>)<sub>3</sub>SiH (13)

$$C_2H_5(CH_3)SiH_2^* \xrightarrow{\text{AMES}} \text{products}$$
(14)

$$\longrightarrow$$
 C<sub>2</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>SiH<sub>2</sub> (15)

Reactions 12 and 14 represent sums of several paths which will be discussed in a subsequent section. An asterisk represents a species with internal energy in excess of that required for a decomposition reaction, and w is the collisional stabilization rate constant. M denotes any bath molecule. All of the ETMS\* was assumed to be collisionally stabilized, since at the lowest pressure used in this study less than 2% of the ETMS\* decomposed.<sup>22</sup>

Singlet methylenes are formed by the initial photodissociation process (1a) and triplet methylenes also may be formed during the initial photodissociation (1b) and by singlet to triplet methylene intersystem crossing.<sup>20,23</sup>

Reactions 2-4 represent the primary insertion reactions of the singlet methylenes. The quantities  $k_2/k_3$ and  $k_4/(k_2 + k_3)$  have been determined previously and are 2.3 and 0.86, respectively.<sup>16</sup> The quantity  $k_4/k_2$  is equal to the high pressure ETMS/TMS ratio. The value of  $k_4/k_2 = 1.28$  from the intercept of Figure 4 is nearly identical with the value 1.23 which was reported earlier.<sup>16b</sup>

Reaction 6 is the abstraction of an H-atom from the silicon atom of DMS by  $CH_2$ . Experimental studies show that it is the  ${}^{3}CH_2$  which abstracts H atoms from carbon.<sup>20, 23-25</sup> It has not been determined that some



Figure 4. Plot of ETMS/TMS vs.  $1/P \text{ (cm}^{-1})$  for TEMS-DMS-CH<sub>2</sub>N<sub>2</sub> photolyses at 3660 Å:  $\Box$ , no scavenger added; O, oxygen added. The line through the ETMS/TMS points with oxygen added was determined by the method of least squares.

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The Journal of Physical Chemistry, Vol. 76, No. 4, 1972

abstraction from silicon is not due to singlet methylenes;<sup>21</sup> therefore the abstracting methylene is designated CH<sub>2</sub>. C-H abstraction by triplet methylenes is not included in the mechanism since there was no methylpropylsilane formed. This compound would be formed by C<sub>2</sub>H<sub>5</sub> + CH<sub>2</sub>SiH<sub>2</sub>CH<sub>8</sub> recombination. The presence of ethyldimethylsilane in this system and no methylpropylsilane implies that C-H abstraction is unimportant. In addition, at 300°K methyl radicals abstract H atoms  $3.6 \times 10^5$  times faster from SiH<sub>4</sub> than from CH<sub>4</sub>,<sup>26</sup> and assuming a similar trend for CH<sub>2</sub> it is reasonable that C-H relative to Si-H abstraction by methylene radicals would be of minor importance in this system.

Reaction 7, which has been proposed previously,<sup>27</sup> was included to account for the formation of ethyl radicals at the higher pressures in this system.

Reaction 8 accounts for the higher TMS/MES and lower ETMS/TMS ratios for 1/P < 2 in the absence of O<sub>2</sub>. The equivalence of the TMS/MES ratios (Figure 1) in the presence and absence of O<sub>2</sub> for 1/P > 2 indicates that reaction 8 becomes relatively less important at lower pressures. The same conclusion can be made from the ETMS/TMS ratios (Figure 3), where the difference between the ETMS/TMS ratios in the presence and absence of O<sub>2</sub> decreases for the experiments performed at the lower pressures. This could be a result of higher concentrations of other radicals at the lower pressures in this system competing with reaction 8 for CH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>SiH radicals.

Reactions 9 and 10 account for the formation of EDMS and  $C_8H_8$  in this reaction system. Reaction 11 is included to allow for the formation of the large amount of  $C_2H_6$  in the absence of a scavenger (Table I).

Si-H abstraction by methyl radicals was not included in the mechanism since the  $CH_4/TMS$  ratios remained unchanged when Bd was added to the reaction mixtures.

Applying the steady state approximation to the  $(CH_8)_2SiH$  radical yields at high pressures the following equation

$$\frac{\text{TMS}^{\text{abs}} + \text{EDMS}}{\text{MES} + \text{TMS}^{\text{ins}}} = \frac{k_6[\text{CH}_2]}{[k_3 + k_2][^{1}\text{CH}_2]}$$
(I)

where TMS<sup>abs</sup> and TMS<sup>ins</sup> signify the TMS formed by abstraction-recombination and insertion, respectively. Inserting the appropriate product ratios into eq I gives

$$\frac{k_6[\text{CH}_2]}{(k_8 + k_2)[^1\text{CH}_2]} = \frac{2.69 - 2.30 + 0.24}{1.00 + 2.30} = 0.19$$

Thus 16% of reaction of methylene radicals with DMS under these conditions is abstraction of an H atom from silicon. This value is slightly smaller than the value of 27% found by Mazac and Simons for reaction with methylsilane.

Unimolecular Decomposition of TMS\* and MES\*.

The Journal of Physical Chemistry, Vol. 76, No. 4, 1972



Figure 5. Plot of TMS/MES  $(1 + k_{\text{TMS}}/w) vs. 1/w (10^{-8} \text{ sec})$  for DMS-CH<sub>2</sub>N<sub>2</sub>-O<sub>2</sub> photolyses at 3660 Å. The line was determined by the method of least squares.

Application of the steady state approximation to TMS<sup>\*</sup> and MES<sup>\*</sup> gives the following two equations for reactions in the presence of a scavenger

$$\frac{\text{ETMS}}{\text{TMS}} = \frac{k_4}{k_2} + \frac{k_{\text{TMS}}}{w} \frac{k_4}{k_2} \tag{II}$$

$$\frac{\text{TMS}}{\text{MES}} \left( 1 + \frac{k_{\text{TMS}}}{w} \right) = \frac{k_2}{k_3} + \frac{k_{\text{MES}}}{w} \frac{k_3}{k_2}$$
(III)

where the ETMS/TMS product ratio has been normalized to a DMS/ETMS reactant ratio of 1.

A plot of the data according to eq II is shown in Figure 4 and the value derived for  $k_{\rm TMS}$  is 2.93  $\pm$  0.47  $\times$  10<sup>7</sup> sec<sup>-1</sup>. A plot of the data according to eq III is presented in Figure 5 from which a value of  $k_{\rm MES} =$  3.30  $\pm$  0.43  $\times$  10<sup>7</sup> sec<sup>-1</sup> is derived.

The following reactions represent possible unimolecular decomposition paths for TMS\* and MES\*

 $(CH_3)_3SiH^* \longrightarrow CH_3 + (CH_3)_2SiH$  (16)

- $\rightarrow$  H + (CH<sub>3</sub>)<sub>3</sub>Si (17)
- $\longrightarrow CH_4 + (CH_3)_2Si$  (18)
- $\rightarrow C_2 H_6 + C H_3 SiH$  (19)
- $C_2H_5(CH_3)SiH_2^* \longrightarrow CH_3 + C_2H_5SiH_2$  (20)
  - $\longrightarrow C_2H_5 + CH_3SiH_2$  (21)
  - $\rightarrow$  H + C<sub>2</sub>H<sub>5</sub>(CH<sub>3</sub>)SiH (22)
  - $\longrightarrow$  H<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>SiCH<sub>3</sub> (23)
  - $\longrightarrow CH_4 + C_2H_5SiH$  (24)
  - $\longrightarrow C_2H_6 + CH_3SiH$  (25)

(25) D. F. Ring and B. S. Rabinovitch, J. Phys. Chem., 72, 191 (1968).

(26) O. P. Strausz, E. Jakubowski, H. S. Sandhu, and H. E. Gunning, J. Chem. Phys., 57, 552 (1971).

(27) (a) G. Z. Whitten and B. S. Rabinovitch, J. Phys. Chem., 69, 4348 (1965); (b) B. M. Herzog and R. W. Carr, Jr., *ibid.*, 71, 2688 (1967); (c) D. F. Ring and B. S. Rabinovitch, Can. J. Chem., 46, 2435 (1968).

Molecular elimination of  $C_{3}H_{8}$  from MES<sup>\*</sup> is not included in the mechanism since  $C_{3}H_{8}$  was not formed in the presence of a scavenger.

A steady-state treatment of the above mechanism leads to the following equations for the molecular elimination processes

$$\frac{\mathrm{CH}_{4}^{(\mathrm{TMS})}}{\mathrm{TMS}} = \frac{k_{13}}{w}$$
(IV)

$$\frac{C_2 H_6^{(TMS)}}{TMS} = \frac{k_{19}}{w}$$
(V)

$$\frac{\mathrm{H}_2}{\mathrm{MES}} = \frac{k_{23}}{w} \tag{VI}$$

$$\frac{\mathrm{CH}_{4}^{(\mathrm{MES})}}{\mathrm{MES}} = \frac{k_{24}}{w}$$
(VII)

$$\frac{C_2 H_6^{(MES)}}{MES} = \frac{k_{25}}{w}$$
(VIII)

where the superscripts (TMS) and (MES) indicate the product is formed by TMS\* and MES\* decomposition, respectively.

CH<sub>4</sub> could be formed by either reaction 18 or 24, and C<sub>2</sub>H<sub>6</sub> could be formed by either reaction 19 or 25. Reaction 18 is the more likely source of CH<sub>4</sub> since: (a) 2.3 times as much TMS\* is formed as MES\*, (b) the ratio of the reaction path degeneracy of reaction 18 to that of reaction 24 is 1.5, (c) TMS\* contains  $\sim$ 7 kcal/ mol more excess energy than MES\* (the difference in the energies of TMS\* and MES\* will be discussed in the subsequent section) and (d) the critical energies and A factors per path for reactions 18 and 24 should be similar. A plot of CH<sub>4</sub>/TMS vs. 1/P is presented in Figure 3, and a least-squares line with the intercept forced through zero gives  $k_{18} = 0.80 \pm 0.09 \times 10^7 \text{ sec}^{-1}$ . This procedure assumes  $k_{24}$  equals zero.

The lack of  $C_3H_3$  formation in the presence of a scavenger suggests that molecular elimination reactions involving two alkyl groups are unimportant for these alkylsilanes relative to the other decomposition paths. Intuitively one would expect these processes to be slow due to tight complex structures. Thus, one would expect reaction 25 to be the major source of  $C_2H_6$  in the presence of a scavenger and not reaction 19.  $k_{19}$  will be taken as zero. Making this assumption, the  $C_2H_6/$ MES ratios are plotted vs. 1/P in Figure 6. The least-squares lines give  $k_{25}$  equal to 0.36  $\pm$  0.04  $\times$  10<sup>7</sup>  $\sec^{-1}$  and 0.61  $\pm$  0.10  $\times$  10<sup>7</sup> sec<sup>-1</sup> for the experiments with O<sub>2</sub> and Bd added, respectively. Comparison of the two sets of data shows that  $0.36 \times 10^7 \text{ sec}^{-1} \text{ prob-}$ ably is the more correct value for  $k_{25}$ , since the data with  $O_2$  present is more reproducible and the  $C_2H_6/$ MES ratios are smaller with added  $O_2$ , indicating that  $O_2$  is the more efficient scavenger.

A possible assumption would be that  $k_{24} \simeq k_{25} = 0.36$  $\times 10^7 \text{ sec}^{-1}$ . Equating  $k_{24}$  with this value for  $k_{25}$  would

Figure 6. Plot of  $C_2H_6/MES$  vs.  $1/P(cm^{-1})$  for DMS-CH<sub>2</sub>N<sub>2</sub> photolyses at 3660 Å:  $\Delta$ , no scavenger added;  $\Box$ , Bd added; and, O, oxygen added. The solid line is a least-squares line through the open circles with the intercept forced to zero and the dashed line is a least-squares line through the squares with the intercept forced to zero.

yield  $k_{18} = 0.65 \times 10^7 \text{ sec}^{-1}$ . The plot of CH<sub>4</sub>/TMS that would result if  $k_{18} = 0.65 \times 10^7 \text{ sec}^{-1}$  is indicated by the dashed line in Figure 3.

Since H<sub>2</sub> formation was not measured with a scavenger present in the reaction mixtures, H<sub>2</sub> could be formed by Si-H abstraction by H atoms. The source of H atoms being reactions 17 and 22. The large excess of methyl radicals in this system relative to H atoms and the lack of evidence for SiH abstraction by CH<sub>3</sub> radicals suggests that Si-H abstraction by H atoms is unimportant. Also, it has been found<sup>28</sup> in this laboratory that chemically activated methylsilane and dimethylsilane produced by silane-diazomethane and methylsilane-diazomethane photolyses at 3660 A decompose almost entirely by molecular elimination, with  $H_2$  elimination being the primary decomposition path in each case. No evidence for Si-H bond rupture was found in these systems. Therefore, the formation of  $CH_4$  and  $C_2H_6$  by molecular elimination reactions in this system suggests that  $H_2$  is also formed by molecular elimination. Assuming H<sub>2</sub> is formed by reaction 23, a plot of  $H_2/MES$  vs. 1/P is given in Figure 2. The least-squares line gives a value for  $k_{23} = 1.37 \pm 0.07 \times$ 10<sup>7</sup> sec<sup>-1</sup>. This represents the maximum value for  $k_{23}$ . If the  $H_2$  were formed entirely by reaction 17,  $k_{17}$  would equal 0.55  $\times$  10<sup>7</sup> sec<sup>-1</sup>.

A summary of the experimental rate constants is presented in Table III.

## Theoretical Calculations

RRKM calculations were performed to determine the A factor for methyl rupture from trimethylsilane and to place some restrictions on the relative importance of the possible decomposition paths for TMS\* and MES\*. The RRKM theory expression for  $k_{E^{*}}$ ,<sup>29,30</sup> the specific dissociation rate at the energy  $E^{*}$ , is

(28) Unpublished results.

		Rate constant, sec -1			
	Process	Exptl <sup>b</sup>	$\operatorname{Calcd}^{c}$		
$(CH_3)_3SiH*$	$\rightarrow$ products	$k_{\rm TMS} = 2.93 \pm 0.47 \times 10^{7}$	$k_{\rm TMS} = 2.93 \times 10^7$		
	$\rightarrow CH_3 + (CH_3)_2SiH$	$1.44 \leqslant k_{16} \leqslant 2.93 \times 10^7$ $[k_{16} = 2.28 \times 10^7]$	$k_{10} = 2.00 \times 10^7$		
	$\rightarrow$ H + (CH <sub>3</sub> ) <sub>3</sub> Si	$k_{17} \leq 0.55 \times 10^{7}$ [ $k_{17} = 0.00$ ]	$k_{17} = 0.20 \times 10^{7}$		
	$\rightarrow CH_4 + (CH_8)_2Si$	$k_{18} \leq 0.80 \times 10^7$ $k_{18} = 0.65 \times 10^7$	$k_{18} = 0.74 \times 10^{7}$		
	$\rightarrow C_2H_6 + CH_3SiH$	$k_{19} \leq 0.14 \times 10^7$ $[k_{19} = 0.00]$	$k_{19} = 0.00$		
$C_2H_5(CH_3)SiH_2*$	→ products	$k_{\rm MES} = 3.30 \pm 0.43 \times 10^7$	$k_{\rm MES} = 3.30 \times 10^7$		
	$\rightarrow$ CH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> SiH <sub>2</sub>	$0 \leq (k_{20} + k_{21}) \leq 3.30 \times 10^7$	$k_{20} = 0.21 \times 10^7$		
	$\rightarrow C_2H_5 + CH_3SiH_2$	$[(k_{20} + k_{21}) = 1.2 \times 10^7]$	$k_{21} = 1.09 \times 10^7$ $[k_{21} = 1.71 \times 10^7]$		
	$\rightarrow$ H + C <sub>2</sub> H <sub>6</sub> (CH <sub>3</sub> )SiH	$(k_{22} + k_{23}) \leqslant 1.37 \times 10^7$ $[k_{22} = 0.00]$	$k_{22} = 0.12 \times 10^7$ $k_{23} = 1.37 \times 10^7$		
	$\rightarrow$ H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> SiCH <sub>3</sub>	$[k_{23} = 1.37 \times 10^7]$	$[k_{23} = 0.75 \times 10^7]$		
	$\rightarrow \mathrm{CH}_4 + \mathrm{C}_2\mathrm{H}_5\mathrm{SiH}$	$k_{24} \leqslant 2.00 \times 10^7$ $[k_{24} = 0.36 \times 10^7]$	$k_{24} = 0.15 \times 10^7$		
	$\rightarrow C_2H_6 + CH_8SiH$	$k_{25} \leqslant 0.36 \times 10^7$ $[k_{25} = 0.36 \times 10^7]$	$k_{25} = 0.36 \times 10^7$		

Table III: Trimethylsilane and Methylethylsilane Unimolecular Rate Constants<sup>a</sup>

<sup>a</sup> The error limits listed are those for a 90% confidence interval. <sup>b</sup> The experimental rate constants given within the brackets are those which result if  $C_2H_6$  and  $H_2$  are formed only by reactions 25 and 23, respectively. CH<sub>4</sub> is formed by reactions 18 and 24, and  $k_{24} = k_{25}$ . <sup>c</sup> RRKM theory calculations in which  $(k_{16} + k_{17} + k_{16})$  was set equal to  $k_{TMS}$  and  $(k_{20} + k_{21} + k_{22} + k_{23} + k_{24} + k_{26})$  was set equal to  $k_{MES}$ .  $k_{19} = 0$  was assumed. The rate constants in brackets are those which result when it is assumed that the H<sub>2</sub> is formed by reactions 17, 22, and 23 instead of only 23.

$$k_{E^*} = dI_r \sum P(E_{vr}^+) / hN(E_{vr}^*)$$
(IX)

where d is the reaction path degeneracy,  $I_r$  is the adiabatic partition function ratio,  $\Sigma P(E_{vr}^+)$  is the sum of all vibrational-internal rotational energy eigenstates for the activated complex up to the energy  $E^+$  ( $E^+ = E^* - E_0$ ), h is Planck's constant, and  $N(E_{vr}^*)$  is the density of the vibrational-internal rotational eigenstates for the activated molecule. A more recent treatment of adiabatic overall rotations gives results identical with the expression above for this particular calculation.<sup>31</sup>

The energy,  $E^*$ , of TMS\* is defined by the equation

$$-E^* = \Delta H_{\rm f}^{\circ}({\rm TMS}) - \Delta H_{\rm f}^{\circ}({\rm DMS}) - [\Delta H_{\rm f}^{\circ}({}^{1}{\rm CH}_{2}) + E^*({}^{1}{\rm CH}_{2})] - E_{\rm th} \quad (X)$$

 $E^{*({}^{1}\mathrm{CH}_{2})}$  is the excess energy carried by  ${}^{1}\mathrm{CH}_{2}$  from the photolysis reaction into TMS\* and  $E_{\mathrm{th}}$  is the average thermal energy of the formed TMS\*. The value for  $[\Delta H_{\mathrm{f}}^{\circ}({}^{1}\mathrm{CH}_{2}) + E^{*}({}^{1}\mathrm{CH}_{2})]$  is 116.1 kcal/mol,<sup>24,32</sup> and  $E_{\mathrm{th}}$ , calculated from statistical thermodynamics, is 3.3 kcal/mol. The difference in the heats of formation of TMS and DMS was determined by the following procedure. Combining reactions 26 and 27

$$(CH_3)_2SiH_2 \longrightarrow (CH_3)_2SiH + H \qquad D^{\circ}_{298}(Si-H)$$
 (26)

 $CH_3 + (CH_3)_2SiH \longrightarrow (CH_3)_3SiH$ 

$$-D^{\circ}_{298}(\text{Si-C})$$
 (27)

The Journal of Physical Chemistry, Vol. 76, No. 4, 1972

leads to the following equation

$$D^{\circ}_{298}(\text{Si-H}) - D^{\circ}_{298}(\text{Si-C}) = \Delta H_{f}^{\circ}_{298}(\text{H}) - \Delta H_{f}^{\circ}_{298}(\text{CH}_{3}) + [\Delta H_{f}^{\circ}_{298}(\text{TMS}) - \Delta H_{f}^{\circ}_{298}(\text{DMS})] \quad (XI)$$

From a survey of the literature<sup>33-35</sup> we derive a value of  $6 \pm 2$  kcal/mol as the most likely difference between the Si-H bond dissociation energy of DMS and the Si-C bond dissociation energy of TMS. Using  $\Delta H_{f}^{\circ}_{298}$ -(H) = 52.0 kcal/mol and  $\Delta H_{f}^{\circ}_{298}$ (CH<sub>3</sub>) = 34.0 kcal/mol,<sup>36</sup> the difference in the heats of formation of TMS and DMS at 298°K is  $-12 \pm 3$  kcal/mol. This is in agreement with the most recent bond additivity determination of this quantity, -11.3 kcal/mol, by Potzinger and Lampe.<sup>37</sup> At 0°K this difference between

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- (32) J. W. Simons and G. W. Taylor, J. Phys. Chem., 73, 1274 (1969);
   G. W. Taylor and J. W. Simons, *ibid.*, 74, 464 (1970).
- (33) W. C. Steele, L. D. Nichols, and F. G. A. Stone, J. Amer. Chem. Soc., 84, 4441 (1962).
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the heats of formation of TMS and DMS is  $-10.5 \pm 3.0$  kcal/mol. The value for  $E^*$ , the energy of TMS\*, is  $130 \pm 3$  kcal/mol.

The critical energy,  $E_0$ , for Si–C bond rupture in trimethylsilane is probably equivalent to the Si–C bond dissociation energy. Steele and coworkers<sup>33</sup> determined a value of 86 kcal/mol for the Si–C bond dissociation energy in methylsilane. Recent electron impact studies by Davidson and coworkers<sup>34</sup> and Lappert, et al.,<sup>36</sup> place the Si–C bond dissociation energy in tetramethylsilane at approximately 76 and 74.5 kcal/mol, respectively. More recently, Davidson and Lampert<sup>13</sup> have measured an activation energy of 76.5 kcal/mol for Si–C bond rupture in trimethylsilane. A value of 78  $\pm$  2 kcal/mol was used for the critical energy in the calculations presented here.

Three activated complex structures were derived to fit the median value for  $k_{16}$ ,  $2.2 \pm 0.8 \times 10^7 \text{ sec}^{-1}$ , with a theoretical rate constant at  $E^* = 130 \text{ kcal/mol}$  and  $E_0 = 76, 78$ , and 80 kcal/mol. In each complex a Si-C stretching vibration was taken as the reaction coordinate and two rocking and two bending motions were each lowered by constant factors until the calculated rate was identical to  $k_{16} = 2.2 \times 10^7 \text{ sec}^{-1}$ . These adjustments are consistent with previous complexes for alkane and alkylsilane decompositions.<sup>22,24</sup> The adjusted vibrational frequencies for the four complex models are given in Table IV. In the calculations all internal rotations in the molecule and activated complexes were treated as free rotors, since the barrier to internal rotation about a C-Si bond is low.<sup>39</sup>

**Table IV:** Activated Complex Models for Si-C Bond Rupturein Trimethylsilane<sup>a,b,e</sup>

Motion	Mole- cule	(	Complex mod II	el
Si–C stretch	714	R.C."	R.C.	R.C.
Si-CH <sub>3</sub> rock	874	404	344	289
Si-CH <sub>3</sub> rock	835	386	329	276
C-Si-C bend	244	113	96	81
C-Si-C bend	225	104	89	75
$\log A^d$		15.3	15.6	15.9

<sup>a</sup>  $I_r = 1.6$  for each complex model, ref 22. <sup>b</sup> The reaction path degeneracy is 3 for each complex. <sup>c</sup> R.C. = reaction coordinate. <sup>d</sup> Theoretical Arrhenius A factors at 1000°K. For calculational procedure see S. Glasstone, K. J. Laidler, and H. E. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941. <sup>e</sup> The vibrational frequencies used for trimethylsilane are by I. F. Kovalev, *Opt. Spectrosc. (USSR)*, 8, 166 (1960).

The calculational results are presented in Table V. Complexes I, II, and III give calculated rates that fit the experimental rate at  $E_0 = 76$ , 78, and 80 kcal/mol, respectively. The A factors for complexes I-III lie in the range  $10^{15.6 \pm 0.3}$  sec<sup>-1</sup> (Table IV). If the uncer-

Table	V:	Calculated	$k_{E^*}$ (sec <sup>-1</sup> ) Values for
Methy	$1 \mathrm{F}$	upture from	Trimethylsilane

•	-	•	
$E_0$	I	Complex models II E* = 130 kcal/mol	III
76 78 80	$2.2 \times 10^{7}$ $1.1 \times 10^{7}$ $0.6 \times 10^{7}$	$4.3 \times 10^{7}$ 2.2 × 10 <sup>7</sup> 1.0 × 10 <sup>7</sup>	$8.5 \times 10^{7}$ $4.4 \times 10^{7}$ $2.2 \times 10^{7}$
	$k_{16} = 2.2$	$2 \pm 0.8 \times 10^{7} \text{ sec}^{-1}$	
	Calculated Va For Complex	lues of $k_{E^*}$ (sec <sup>-1</sup> ) vs II and $E_0 = 78$ kcal/ $k_{E^*}$ se	. E* /mol
	14	··· 1 / ···	
	123	6.80  imes	106
	124	8.13 imes	106
	125	9.68 imes	1.06
	126	$_{1.15} imes$	107
	127	$1.36 \times$	107
	128	1.60 imes	107
	129	1.88  imes	107
	130	$_{2.20} imes$	107
	131	2.57  imes	( 107
	132	$3.00 \times$	107
	133	$3.48 \times$	107

tainties in  $E^*$  and the experimental rate constant were included in the calculations, complex structures giving A factors in the range of  $10^{15.0}-10^{16.2}$  sec<sup>-1</sup> would fit these chemical activation results, in agreement with  $10^{15.9 \pm 0.7}$  sec<sup>-1</sup>, reported by Davidson and Lambert.<sup>13</sup> This A factor also agrees with those which have been calculated for methyl rupture in tetramethylsilane<sup>16b</sup> and ethyltrimethylsilane,<sup>40</sup>  $10^{15.0 \pm 0.6}$  sec<sup>-1</sup> and  $10^{15.8 \pm 0.6}$  sec<sup>-1</sup>, respectively.

The relative importance of reactions 16-25 depends in part on the difference in the energies of TMS\* and MES\*. The energy of MES\* is defined by an equation identical with eq X except  $\Delta H_{f}^{\circ}(\text{MES})$  replaces  $\Delta H_{\rm f}^{\circ}({\rm TMS})$ . The difference in the heats of formation of DMS and MES was determined by the following procedure. The difference in the heats of formation of twenty related compounds,  $\Delta H_{f}^{\circ}(CH_{3}X) - \Delta H_{f}^{\circ}$ - $(C_2H_5X)$ , gave an average value of  $3.5 \pm 0.5$  kcal/mol, the substituent group varied from alkyl, alkenyl, and alkynyl to  $NH_2$  and O=COH. Using this value, the energy of MES\* is 122.9 kcal/mol. Thus TMS\* contains  $\sim 7$  kcal/mol more internal energy than MES\*. The data in Table V show that a change in  $E^*$  of 7 kcal/mol lowers the rate constant for methyl rupture from trimethylsilane by a factor of 3.2.

In order to make a qualitative comparison of calculated rate constants for reactions 16–25, which fit the

The Journal of Physical Chemistry, Vol. 76, No. 4, 1972

<sup>(38)</sup> M. F. Lappert, J. Simpson, and T. R. Spalding, J. Organometal. Chem., 17, 1 (1969).

<sup>(39)</sup> J. R. Durig, S. M. Craven, and J. Bragin, J. Chem. Phys., 52, 2046 (1970); 53, 38 (1970).

<sup>(40)</sup> W. L. Hase and J. W. Simons, J. Organometal. Chem., 32, 47 (1971).

experimental results presented in this study, the following two approximations were made: (1) that similar decomposition paths for TMS\* and MES\* have rate constants which differ by a factor of 3.2 per path, and (2) the ratio,  $k_{16}/k_{17}$ , can be derived from the Arrhenius parameters determined by Davidson and Lambert<sup>13</sup> for Si-C and Si-H bond rupture in trimethylsilane. The first approximation assumes identical critical energies and A factors per path for similar decomposition modes. The validity of the second approximation depends on the validity of Davidson and Lambert's data. The agreement between our calculated A factor and theirs

Table VI:Complex Models for Si-C and Si-H Bond Rupturein Trimethylsilane Derived from Experimental A factors<sup>a</sup>

	Si-C Bond rupture <sup>b</sup>		
Motion	Molecule	Complex	
Si–C stretch	714	R.C.	
Si-CH <sub>3</sub> rock	874	282	
Si–CH <sub>3</sub> rock	835	269	
C-Si-C bend	244	79	
C-Si-C bend	225	73	
	$\log A^d = 15.9$	$E_{\rm a} = 76.5$	
		kcal/mol	
	$k_{E^*}$ (130 kcal/mol) =		
	7.2  imes 10	$0^7 \operatorname{sec}^{-1}$	
	SiH Bond Rupture		
Motion	Molecule	Complex	
Si-H stretch	2118	R.C.	
H-Si-C bend	914(2)	92(2)	
	$\log A^d = 15.6$	$E_{\rm a} = 80.3$	
		$\mathbf{keal}/\mathbf{mol}$	
	$k_E*(130 \text{ kcal/mol}) =$	$7.2 imes10^{6}~{ m sec^{-1}}$	

<sup>a</sup> For these calculations  $E_{\rm a}$  was assumed to equal  $E_{0}$ . <sup>b</sup>  $I_{\rm r} = 1.6$ . <sup>c</sup> $I_{\rm r} = 1.0$ . <sup>d</sup> The complex structures were determined using this A factor at a temperature of 1000°K, the median of Davidson and Lambert's study.<sup>13</sup>

for Si-C bond rupture in trimethylsilane supports the second approximation. The first approximation gives  $k_{18}/k_{24} = 4.8$ ,  $k_{16}/k_{20} = 9.6$  and  $k_{17}/k_{26} = 1.6$ . To satisfy the second approximation, complex models were chosen that fit Davidson and Lambert's<sup>13</sup> Arrhenius A factors and are given in Table VI. The calculated values of  $k_{16}$  and  $k_{17}$  are presented in Table VI and  $k_{16}/k_{17} = 10.00$ . Rate constants which result from making these two approximations are given in Table III. The calculated rate constants in brackets for reactions 21 and 23 are those which result when it is assumed that the H<sub>2</sub> measured in these experiments is formed by reactions 17, 22, and 23 instead of only 23.

We are not suggesting that these various rate constants are correct as to absolute values but their relative sizes do indicate which paths are the important decomposition paths for TMS\* and MES\*. The results show that  $CH_3$  rupture is the most probable decomposition path for TMS\* and  $H_2$  molecular elimination and  $C_2H_5$ rupture are the most probable decomposition paths for MES\*.

The formation of  $CH_4$  by molecular elimination from TMS\*, as the data implies, does not contradict the proposal of Davidson and Lambert that at 1000°K trimethylsilane decomposes entirely by Si-C and Si-H bond rupture. If the A factor and critical energy for reaction 16 are assumed to equal  $10^{15.6}$  sec<sup>-1</sup>, and 78 kcal/mol, respectively (Tables IV and V), the following sets of A factors and critical energies for reaction 18 yield the minimum value of  $k_{16}/k_{18}$  3.0 (Table III):  $10^{15.7}$  sec<sup>-1</sup>, 82 kcal/mol;  $10^{15.4}$  sec<sup>-1</sup>, 80 kcal/mol;  $10^{15.1} \text{ sec}^{-1}$ , 78 kcal/mol;  $10^{14.8} \text{ sec}^{-1}$ , 76 kcal/mol; and  $10^{14.5}$  sec<sup>-1</sup>, 74 kcal/mol. None of these sets of A factors and activation energies agree exactly with that measured by Davidson and Lambert<sup>13</sup> for CH<sub>4</sub> formation and indicate that they were probably correct in associating their Arrhenius parameters with Si-C bond rupture.