

# Chemically Activated Tetramethylsilane from the Reaction of Singlet Methylene Radicals with Trimethylsilane

W. L. Hase and J. W. Simons

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and this with (A29) and (A30) requires that

$$\Omega_{aa}^{(a)}(\mathbf{r}_i, \mathbf{r}_j) = \Omega_{bb}^{(b)}(\mathbf{r}_i, \mathbf{r}_j) = 0.$$
(B22)

These together with (A22) and (A25) lead to

$$\Omega_{\nu\mu}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \Omega_{\nu\mu}^{(0)}(\boldsymbol{r}_i, \boldsymbol{r}_j) = \Omega(\boldsymbol{r}_{ij}), \qquad (B23)$$

which states that the potential of mean force for the binary isotopic mixture is independent of the species.

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# Chemically Activated Tetramethylsilane from the Reaction of Singlet Methylene **Radicals with Trimethylsilane\***

W. L. HASE<sup>†</sup> AND J. W. SIMONS

Chemistry Department, New Mexico State University, Las Cruces, New Mexico 88001

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An experimental study of the photolysis of trimethylsilane-diazomethane-oxygen mixtures and tetramethylsilane-trimethylsilane-diazomethane-oxygen mixtures at 4358 and 3660 Å is reported. Experimental rate constants for the decomposition of chemically activated ethyl trimethylsilane, ethyl dimethylsilane, and tetramethylsilane are determined. These specific rates range from  $3 \times 10^4$  sec<sup>-1</sup> to  $6.5 \times 10^5$  sec<sup>-1</sup>. A comparison of the 4358- and 3660-Å rate constants for tetramethylsilane decomposition with RRKM theory calculations suggest that a thermal A factor of  $10^{15.0\pm0.5}$  sec<sup>-1</sup> is correct for primary decomposition by Si-C bond rupture. The uncertainty in this A factor reflects the uncertainties in the  $E^*$  and  $E_0$  values for chemically activated tetramethylsilane. A discussion of this A factor relative to that found previously for neopentane decomposition is given.

#### INTRODUCTION

It recently has been shown that singlet methylene radicals insert into the Si-H bonds of methylsilane to form chemically activated dimethylsilane.<sup>1</sup> The relative contributions of various reaction paths to the total decomposition of chemically activated dimethylsilane is uncertain. This uncertainty doesn't exist in a study of chemically activated tetramethylsilane, which can be produced by the insertion of a singlet methylene radical into the Si-H bond of trimethylsilane since the reaction path giving Si-C bond rupture is almost certainly of primary importance.

This work was undertaken in the hope that a comparison of the experimental rate constants for the unimolecular decomposition of chemically activated tetramethylsilane with those calculated by Rice-Ramsperger-Kassel-Marcus (RRKM) rate theory would give valuable information about the activated complex structure and energetics for tetramethylsilane decomposition. The activated complex that fits the chemical activation data can be used to calculate the Arrhenius A factor for tetramethylsilane decomposition.

#### EXPERIMENTAL

#### Materials

Diazomethane was prepared by the reaction of Nmethyl-N-nitroso-p-toluenesulfonamide with a saturated solution of KOH in 1,4-butanediol and was stored in di-*n*-butylphthalate at liquid nitrogen temperature.

Trimethylsilane was prepared in vacuo by the reaction of trimethylchlorosilane with LiAlH<sub>4</sub> in dibutyl ether and was purified by gas-liquid chromatography.

4004

NMR Specialties tetramethylsilane (purity 99.9%) was used without further purification.

#### Apparatus and Procedure

All gas-handling was performed with a conventional high vacuum system containing greaseless valves. 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 5860 filter. The 4348-Å line was isolated by a combination of Esco Products 5850 and 3389 filters.

Mixtures of diazomethane and trimethylsilane, and of diazomethane, trimethylsilane, and tetramethylsilane with added oxygen were photolyzed for times varying from 2 h at high pressures and up to 30 h at the lower pressures. The low pressure experiments were loaded through a trap at 0°C in order to reduce the pressure of mercury in the reaction vessel. The ratio of diazomethane to reactants was usually 1.5:10, but no variation in product proportions resulted when this ratio was varied from 1:10 to 3:10. The volume of the reactors varied from 19–21 400 cc. No surface effects were observed by varying reactor volumes for experiments at the same pressure. Dark reactions at different pressures gave only those products due to decomposition of diazomethane.

### ANALYSIS

The quantitative analyses of the condensable products at  $-196^{\circ}$ C were done by gas-liquid phase chromatography (glpc). The analytical column used consisted of 25 ft of 30% dibutylphthalate on Chromosorb followed by 4 ft of didecylphthalate on Chromosorb. A mixture of trimethylsilane, tetramethylsilane, and ethyldimethylsilane was used to calibrate the column for the ethyldimethylsilane to tetramethylsilane ratios (EDMS/TEMS). Since the calibration factor for ethyltrimethylsilane cancels out in the calculation of the rate constants, peak height×retention time ratios are given for the ethyltrimethylsilane to ethyldimethylsilane ratios (ETMS/EDMS).

The products were identified by mass spectra and glpc retention times compared with those of known samples.

### RESULTS

Two different systems were studied in order to determine the decomposition rate constant for tetramethylsilane (TEMS). In one system tetramethylsilane-trimethylsilane-diazomethane-oxygen mixtures were photolyzed at 4358 and 3660 Å. The ratio of the two alkylsilane products, ethyltrimethylsilane and ethyldimethylsilane, were measured and are given in Table I. In the second system mixtures of trimethylsilane, diazomethane, and oxygen were photolyzed. The measured ratios of the two alkylsilane products, ethyldimethylsilane and tetramethylsilane, are given in Table II. The amount of tetramethylsilane decomposition can

TABLE I. The tetramethylsilane-trimethylsilanediazomethane-oxygen system.<sup>a</sup>

P <sub>tems</sub>	P <sub>TRM S</sub>	$P_{\rm CH_{2N_{2}}}$	P02	ETMS/EDMS <sup>b</sup>					
Photolyses at 3660 Å									
3.40	3.44	1.67	1.38	1.69					
1.47	1.50	0.61	0.71	1.76					
0.54	0.58	0.21	0.22	1.74					
0.43	0.43	0.17	0.19	1.78					
0.21	0.21	0.063	0.093	1.77					
0.11	0.14	0.049	0.062	1.79					
0.083	0.127	0.033	0.039	1.82					
0.084	0.084	0.036	0.036	1.92					
0.072	0.072	0.039	0.037	1.93					
0.069	0.066	0.018	0.025	1.97					
0.058	0.069	0.019	0.021	1.89					
0.038	0 077	0.016	0.020	2.00					
0.053	0.053	0.018	0.020	1.90					
0.040	0.034	0.037	0.035	1.98					
0.015	0.036	0.014	0.019	2.04					
0.000	0.020	0.011	0.012	2.02					
0.022	0.029	0.010	0.012	2.02					
0.020	0.025	0.010	0.010	2.00					
0.020	0.025	0.010	0.010	2.15					
0.022	0.025	0.010	0.010	2.13					
0.010	0.020	0.010	0.009	2.33					
	$\mathbf{P}^{\mathbf{h}}$	otolyses at 4	358 Å						
27.7	29.6	10.4	5.0	1.73					
2.93	4.18	0.84	1.15	1.75					
1.71	1.65	0.45	0.57	1.76					
0.48	0.53	0.13	0.23	1.79					
0.19	0.20	0.066	0.063	1.84					
0.14	0.14	0.051	0.038	1.75					
0.14	0.14	0.038	0.051	1.78					
0.11	0.11	0.038	0.034	1.89					
0.081	0.084	0.026	0.024	1.84					
0.047	0.047	0.022	0.014	1.98					
0.038	0.041	0.012	0.015	1.88					
0.038	0.042	0.009	0.009	1.89					
0.033	0.034	0.017	0.014	1.92					
0.028	0.028	0.011	0.012	2.02					
0.024	0.023	0.012	0.012	2.07					
0.019	0.020	0.012	0.015	2.06					
0.018	0.019	0.006	0.007	2.09					
0.016	0.018	0.008	0.006	2.02					
0.017	0.018	0.005	0.009	2.09					
0.015	0.016	0.006	0.005	2.07					
0.011	0.015	0.005	0.003	2.16					
0.009	0.012	0.006	0.004	2.19					
0.007	0.012	0.007	0.004	2.24					
0.007	0.011	0.006	0.005	2.38					
0.005	0.013	0.006	0.005	2.40					
0.006	0.010	0.004	0.004	2.44					

<sup>a</sup> All pressures are in torr.

<sup>b</sup> This product ratio has been normalized to a reactant ratio of 1.0.

be determined by comparing the ethyltrimethylsilane to ethyldimethylsilane ratios (ETMS/EDMS) in the first system to the ethyldimethylsilane to tetramethylsilane ratios (EDMS/TEMS) in the second system at the same pressures.

TABLE II. The trimethylsilane-diazomethane-oxygen system.\*

P <sub>TRM S</sub>	$P_{\mathbf{CH}_{2}\mathbf{N}_{2}}$	$P_{\mathbf{0_2}}$	EDMS/TEMS				
Photolyses at 3660 Å							
4.41	0.98	1.02	1.25				
2.19	0.63	0.67	1.25				
0.94	0.29	0.35	1.26				
0.54	0.12	0.11	1.24				
0.28	0.088	0.075	1.26				
0.19	0.081	0.088	1.23				
0.22	0.043	0.070	1.25				
0.22	0.032	0.029	1.25				
0.18	0.039	0.042	1.25				
0.14	0.020	0.020	1.27				
0.099	0.021	0.018	1.28				
0.082	0.017	0.017	1.30				
0.064	0.017	0.016	1.36				
0.061	0.010	0.010	1.37				
0.049	0.015	0.016	1.30				
	Photolyses	s at 4358 Å					
41.00	6.22	8.00	1.24				
2.18	0.36	0.57	1.24				
1.48	0.36	0.47	1.31				
1.47	0.18	0.23	1.27				
0.68	0.089	0.089	1.28				
0.25	0.031	0.040	1.25				
0.19	0.019	0.028	1.29				
0.12	0.023	0.021	1.28				
0.072	0.012	0.012	1.28				
0.047	0.011	0.007	1.34				
0.051	0.006	0.009	1.27				
0.032	0.006	0.006	1.31				
0.023	0.006	0.005	1.32				
0.020	0.006	0.006	1.35				

<sup>a</sup> All pressures are in torr.

The following reaction scheme accounts for the products formed in the trimethylsilane-diazomethane-oxygen system:

$$CH_2N_2 \rightarrow {}^{h\nu}CH_2 + N_2,$$
 [1]

<sup>*K*<sub>2</sub></sup> <sup>*K*<sub>2</sub></sup> (CH<sub>3</sub>)<sub>3</sub>SiH
$$\rightarrow$$
 (CH<sub>3</sub>)<sub>4</sub>Si<sup>\*</sup>, [2]

$$(CH_3)_4Si^{W_3} \rightarrow (CH_3)_4Si,$$
 [3]

$$(CH_3)_4Si^* \rightarrow CH_3 + (CH_3)_3Si, \qquad [4]$$

<sup>*K*<sub>5</sub></sup>  
<sup>1</sup>CH<sub>2</sub>+(CH<sub>3</sub>)<sub>3</sub>SiH
$$\rightarrow$$
C<sub>2</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>SiH\*, [5]

$$C_2H_5(CH_3)_2SiH^{*} \rightarrow C_2H_5(CH_3)_2SiH,$$
 [6]

$$C_{2}H_{5}(CH_{3})_{2}SiH^{*} \rightarrow decomposition.$$

mixture the following reactions must be included in the reaction scheme:

K10

$$^{1}\mathrm{CH}_{2} + (\mathrm{CH}_{3})_{4}\mathrm{Si} \xrightarrow{K_{8}} \mathrm{C}_{2}\mathrm{H}_{5}(\mathrm{CH}_{3})_{3}\mathrm{Si}^{*},$$
 [8]

$$C_2H_5(CH_3)_3Si^* \rightarrow C_2H_5(CH_3)_3Si (ETMS), [9]$$

$$C_2H_5(CH_3)_3Si^* \rightarrow decomposition.$$
 [10]

Only the reactions of singlet electronic state methylene radicals are considered here since the added oxygen scavenges triplet methylene radicals<sup>2</sup> and doublet radicals which are formed by decomposition of the excited species.<sup>3-9</sup> An asterisk denotes excess vibrational-internal rotational energy. The W's are collisional stabilization rate constants and, assuming unit collisional deactivation efficiency, are taken to be the appropriate collision frequencies of the various excited molecules.

Application of the steady state approximation to Reactions [2]-[10] leads to Eqs. (1) and (2) for the two systems studied:

$$\frac{P_{\text{TRMS}}}{P_{\text{TEMS}}} \frac{(\text{ETMS})}{(\text{EDMS})} \left(1 + \frac{K_{10}}{W_9}\right) = \frac{K_8}{K_5} + W_6^{-1} \frac{K_8 K_7}{K_5}, \quad (1)$$

$$\frac{\text{EDMS}}{\text{TEMS}} \left( 1 + \frac{K_7}{W_6} \right) = \frac{K_5}{K_2} + W_3^{-1} \frac{K_5 K_4}{K_2}, \qquad (2)$$

where P is the pressure of the appropriate reactant.

A plot of the left-hand side of Eq. (1) against  $W_6^{-1}$ should be linear and the rate constant for EDMS\* decomposition,  $K_7$ , would be given by the slope divided by the intercept. The rate constant for ETMS\* decomposition,  $K_{10}$ , was approximated by adjusting its value to give the best linear fit of the data to Eq. (1). The values obtained for  $K_{10}$  were  $5 \times 10^4$  sec<sup>-1</sup> at 3660 Å and  $3 \times 10^4$  sec<sup>-1</sup> at 4358 Å. Using these values for  $K_{10}$ , the data plotted according to Eq. (1) are given in Figs. 1 and 2 for the 3660- and 4358-Å photolyses, respectively. The solid lines in Figs. 1 and 2 are the "least squares" lines through the data. The dashed lines in Figs. 1 and 2 are the "least squares" lines through the data when it was assumed that there was no ETMS\* decomposition. By letting  $K_{10}$  vary over reasonable uncertainty limits,  $K_7$  was calculated to be  $4.3 \pm .5 \times 10^{5} \text{ sec}^{-1}$  at 3660 Å and  $2.2 \pm .3 \times 10^{5} \text{ sec}^{-1}$  at 4358 Å.

The unimolecular rate constant for TEMS\* decomposition was determined from Eq. (2). In Figs. 3 and 4 plots of Eq. (2), using the values of  $K_7$  determined above, are given for the 3660- and 4358-Å photolyses, respectively. From the slopes and intercepts of the "least squares" lines in Figs. 3 and 4, the unimolecular rate constant,  $K_4$ , for TEMS\* decomposition was found to be  $6.5\pm0.5\times10^5$  sec<sup>-1</sup> at 3660 Å and  $2.8\pm0.3\times10^5$  sec<sup>-1</sup> at 4358 Å. A summary of the experimental rate constants is given in Table III.

The calculation of the various collision frequencies in Eqs. (1) and (2) required values for the molecular di-

[7]

FIG. 1. Plot of

$$\frac{P_{\text{TRM8}}}{P_{\text{TEM8}}} \frac{(\text{ETMS})}{(\text{EDMS})} \left(1 + \frac{K_{10}}{W_9}\right) \text{vs}^{\texttt{t}} W_6^{-1}$$

for photolyses at 3660 Å, setting  $K_{10}$  equal to  $5 \times 10^4$  sec<sup>-1</sup>. The dashed line represents the "least squares" of the data when  $K_{10}=0$ .





FIG. 2. The same as Fig. 1 except for the 4358-Å data with  $K_{10}=3\times10^4$  sec<sup>-1</sup>. The dashed line has the same meaning as in Fig. 1.

TABLE III.	Summary	of t	he experimental	rate	constants.
------------	---------	------	-----------------	------	------------

A -4: - 4 - 1		W	Experimental rate constants <sup>a,b</sup>		
 Activated molecule	Reaction	(Å)	(torr)	(sec <sup>-1</sup> )	
TEMS	CH₂+(CH₃)₃SiH	3660	0.025	6.5±0.5×10 <sup>5</sup>	
TEMS	CH2+(CH3)3SiH	4358	0.011	2.8±0.3×10⁵	
EDMS	CH <sub>2</sub> +(CH <sub>3</sub> ) <sub>3</sub> SiH	3660	0.017	4.3±0.5×10⁵	
EDMS	CH <sub>2</sub> +(CH <sub>3</sub> ) <sub>3</sub> SiH	4358	0.009	$2.2 \pm 0.3 \times 10^{5}$	
ETMS	$CH_2 + (CH_3)_4Si$	3660	0.002	5×10 <sup>4</sup>	
ETMS	CH <sub>2</sub> +(CH <sub>3</sub> ) <sub>4</sub> Si	4358	0.001	3×10 <sup>4</sup>	

<sup>a</sup> Rate constants in torr units refer to the average bath pressure at which a half of the activated molecules are stabilized.

 $^{\rm b}$  The rate constants for ethyltrimethylsilane are accurate to within about a factor of 2.

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ameters of the various alkylsilanes. Since molecular diameters have not been measured for the alkylsilanes, they were approximated here by assuming that a Si atom contributes as much to the collision diameter of a molecule as two carbon atoms in an alkane. The Lennard-Jones collision diameters for the alkanes were determined by the method described by Rabinovitch *et al.*<sup>10,11</sup> The effective pressure of oxygen was taken to be 0.25 of the measured pressure due to its lower collisional deactivation efficiency.<sup>12</sup> The collision diameters used are listed in Table IV.

#### DISCUSSION

#### Energetics

The average energy  $E^*$  of TEMS<sup>\*</sup> in this system is given by

$$E^* = -\left[\Delta H^{\circ}_{f0}(\text{TEMS}) - \Delta H^{\circ}_{f0}(\text{TRMS})\right] + \left[\Delta H_{f0}^{\circ}(\text{CH}_2) + E^*(\text{CH}_2)\right] + E_{\text{th}}, \quad (3)$$

where  $E^*(CH_2)$  is the excess energy carried by the singlet methylene radical from the photolysis reaction

Table IV. (	Collision	diameters.
-------------	-----------	------------

Molecule	Diametera	
Trimethylsilane	7.22	
Tetramethylsilane	8.64	
Ethyltrimethylsilane	9.38	
Diazomethane	6.55	
Oxygen	4.55	

<sup>a</sup> Diameters are given in angstroms.

into the insertion product, TEMS\*, and  $E_{th}$  is the average thermal energy of TEMS\*. The value of  $\Delta H^{\circ}_{f0}(CH_2) + E^{*}(CH_2)$  is 112.6 kcal/mole at 4358 Å and 116.1 kcal/mole at 3660 Å as determined from diazomethane-cis-butene-2 photolyses.13 The assumption that  $E^*(CH_2)$  is the same in both systems is reasonable since methylene radicals react efficiently with both trimethylsilane and *cis*-butene-2.<sup>14</sup> The value of  $E_{\rm th}$  was calculated from statistical thermodynamics to be 4.3 kcal/mole. The heats of formation of TEMS and TRMS have been determined experimentally by Davidson<sup>15</sup> and by Tannenbaum,<sup>16</sup> and calculated by bond additivity methods.<sup>17-19</sup> The values determined by Tannenbaum and Davidson seem to be in approximate agreement,<sup>20</sup> while there are inconsistencies in the values calculated by bond additivity methods.<sup>21</sup> Therefore,



FIG. 4. The same as Fig. 3 except for 4358-Å photolyses with  $K_7 = 2.2 \times 10^{5} \text{ sec}^{-1}$ .

values of  $-[\Delta H^{\circ}_{f0}(\text{TEMS}) - \Delta H^{\circ}_{f0}(\text{TRMS})]^{22}$  derived from the measurements of Davidson, and of Tannenbaum, were used to establish upper and lower limits for this quantity in the determination of  $E^*$ . Using the value of 11.5 kcal/mole,  $E^*$  is 131.9 kcal/mole at 3660 Å and 128.4 kcal/mole at 4358 Å, and for the value of 7.5 kcal/mole  $E^*$  is 127.9 kcal/mole and 124.4 kcal/mole for the two photolysis wavelengths.

The critical energy  $E_0$  for tetramethylsilane decomposition is probably equivalent to the dissociation energy for a Si–C bond. An early estimate of the average Si–C bond strength was 72 kcal/mole.<sup>23</sup> Hess *et al.*,<sup>24</sup> estimated the Si–C bond dissociation energy in tetramethylsilane at 85 kcal/mole by an electron impact study, but it is believed that this value is too high.<sup>25</sup> Recent electron impact studies by Davidson<sup>15</sup> and coworkers and Lappert *et al.*<sup>26</sup> place the Si–C bond dissociation energy in tetramethylsilane at approximately 76 and 74.5 kcal/mole, respectively. These values are in good agreement with a 1937 measurement of the activation energy for tetramethylsilane decomposition.<sup>27</sup>

Mode	w (cm <sup>-1</sup> )
C–H sym. stretch	2919(4)
CH <sub>2</sub> sym. def.	1254
Si–C skel. stretch	598, 696 (3)
C-H unsym. stretch	2963(2), 2967(6)
CH <sub>3</sub> nonsym. def.	1430(8)
CH <sub>3</sub> rocking	869(8)
C-Si-C skel. def.	202(2), 239(3)
CH <sub>a</sub> sym. def.	1253(3)
Si-CH <sub>3</sub> torsion	Free rotor (4)
$E_z = 89.5$ kcal/mole	

TABLE V. Vibrational frequencies for tetramethylsilane.

A value of  $76\pm 2$  kcal/mole was used in our theoretical calculations for the critical energy.

## **Theoretical Calculations**

The RRKM formulation for  $K_E$ <sup>28</sup> the specific unimolecular dissociation rate constant at the energy E, is given by

$$K_{E} = (I_{r}/h) \left[ \sum_{0}^{E^{+}} P(E^{+}_{vr}) / N(E^{*}_{vr}) \right], \qquad [4]$$

where  $I_r$  is the partition function ratio for the adiabatic degrees of freedom, and includes reaction path degeneracy,

$$\sum_{0}^{E^+} P(E^+_{vr})$$

is the sum of vibrational-internal rotational states for the activated complex at an energy  $E^+$ , and  $N(E^*_{vr})$ is the density of the vibrational-internal rotational states for the molecule at an energy  $E^*$ . The sum and density terms for the molecule and activated complexes were evaluated on a CDC-3300 computer using the approximation of Whitten and Rabinovitch.<sup>29,30</sup>

The vibrational frequencies for the tetramethylsilane molecule<sup>31</sup> are given in Table V. In the molecule, as in

<sup>d</sup> r.c. = reaction co-ordinate.

P	Complex models							
L <sub>0</sub> (kcal/mole)	I	II	III	IV				
	E*=:	131.9 kcal/m	ole					
74	5.7×10 <sup>5</sup>	1.22×10 <sup>6</sup>	2.37×10 <sup>6</sup>	5.23×10 <sup>6</sup>				
76	2.80×10 <sup>5</sup>	5.89×10 <sup>5</sup>	1.16×10 <sup>6</sup>	2.53×10 <sup>6</sup>				
78	$1.37 \times 10^{5}$	2.84×10 <sup>5</sup>	$5.52 \times 10^{5}$	1.22×106				
$Exptl = 6.5 \times 1$	$0^{5} \sec^{-1} (366)$ $E^{*} = 1$	0 Å) 128.4 kcal/m	nole					
$Exptl = 6.5 \times 1$	$0^{5} \sec^{-1} (366)$ $E^{*} = 1$ $3.18 \times 10^{5}$	0 Å) 128.4 kcal/m 6.59×10⁵	nole 1.29×106	2.77×10 <sup>6</sup>				
2xptl=6.5×1 74 76	$0^{5} \sec^{-1} (366)$ $E^{*} = 1$ $3.18 \times 10^{5}$ $1.50 \times 10^{5}$	0 Å) 128.4 kcal/m 6.59×10⁵ 3.11×10⁵	nole 1.29×10 <sup>6</sup> 6.12×10⁵	2.77×10° 1.34×10°				

the activated complexes, the four internal rotations are treated as free rotors since the potential barrier to internal rotation is low, 1.4 kcal/mole,<sup>31</sup> and the excitation energy  $E^*$  is quite large.

Calculations are presented here for four tetramethylsilane activated complex models. In each complex the internal rotations were treated as free rotors, a Si-C stretching vibration was taken as the reaction coordinate, and one Si-C bond length in the activated complex was made 1.7 times its length in the molecule. Two C-Si-C skeletal deformations and two methyl rocking frequencies were lowered by various amounts in the activated complex models. These frequency adjustments are consistent with adjustments that have been made in activated complex models for alkane decom-

TABLE VIII. Calculated  $K_{\mathbf{B}}$  (per second) values for tetramethylsilane decomposition.

TABLE VI. Vibrational parameters for the activated complex models. <sup>a,b</sup>					F		Complex models			
					E <sub>0</sub> (kcal/mole)	I	II	III	IV	
Complex model				$E^* = 127.9$ kcal/mole						
Motion	Molecule	1	2	3	4	74	3.15×10 <sup>5</sup>	6.50×10⁵	1.27×10 <sup>5</sup>	2.81×10 <sup>6</sup>
						76	$1.45 \times 10^{5}$	$3.00 \times 10^{5}$	$5.93 \times 10^{5}$	$1.28 \times 10^{6}$
CH₃ rocking	869(2)	660(2)	563(2)	417(2)	374(2)	78	6.75×104	1.39×10 <sup>5</sup>	2.72×10 <sup>5</sup>	5.97×10 <sup>5</sup>
C-Si-C skel. def.	202	158	121	107	82					
C-Si-C skel. def.	239	189	142	127	91	$Exptl = 6.5 \times 1$	10 <sup>5</sup> sec <sup>-1</sup> (366	0 Å)		
Si–C skel. stretch logA °	696	r.c. <sup>d</sup> 14.5	г.с. 14.8	r.c. 15.2	r.c. 15.5	•	E*=	124.4 kcal/n	nole	
					<u> </u>	74	$1.74{ imes}10^{5}$	3.61×10 <sup>5</sup>	$7.03 \times 10^{5}$	1.55×10 <sup>6</sup>
<sup>a</sup> The ratio of par	tition functi	ons for th	ne over-all	rotational	degrees of	76	$7.44 \times 10^{4}$	$1.56 \times 10^{5}$	3.00×10 <sup>5</sup>	6.58×10 <sup>5</sup>
freedom was calculat <sup>b</sup> The reaction pat	ted to be 1.6 h degeneracy	for each o y is four fe	of the com or each cor	plex mode nplex.	ls.	78	3.32×104	6.85×104	1.34×10 <sup>5</sup>	2.92×10 <sup>5</sup>
<sup>e</sup> Theoretical Arrh	enius A fact	ors (secon	d-1) at 10	00°K.		$Exptl = 2.8 \times 1$	10 <sup>5</sup> sec <sup>-1</sup> (435	8 Å)		

TABLE VII. Calculated  $K_E$  (per second) values for tetramethylsilane decomposition.

position.<sup>32–34</sup> The adjusted vibrational frequencies for the four complex models are given in Table VI.

The calculational results for TEMS\* decomposition at 3660 and 4358 Å are given for the larger set of  $E^*$ values in Table VII and are given for the smaller set of  $E^*$  values in Table VIII. For the  $E^*$  values in Table VII it is seen that complexes I, II, and III give calculated rates at  $E_0 = 74$ , 76, and 78 kcal/mole, respectively, in satisfactory agreement with both the 3660 and 4358 Å experimental results. For the  $E^*$  values in Table VIII it is seen that complexes II, III, and IV give calculated rates at  $E_0 = 74$ , 76, and 78 kcal/mole, respectively, in satisfactory agreement with both the 3660- and 4358-Å experimental results. It is apparent that, within the limits of the reasonable uncertainties in  $E^*$  and  $E_0$  given here, activated complexes giving thermal A factors<sup>35</sup> in the range  $10^{14.5-1}0^{15.5}$  sec<sup>-1</sup> (Table VI) fit the experimental chemical activation results of the study.

The thermal decomposition of tetramethylsilane has been studied manometrically by Helm and Mack.<sup>27</sup> First-order kinetics were found over the temperature range 660–720°C giving Arrhenius parameters of A = $10^{15.2}$  sec<sup>-1</sup> and  $E_a = 79$  kcal/mole. These thermal parameters are in remarkable agreement with the results of this study.

The range of A factors determined here for tetramethylsilane decomposition are smaller than the Afactors that have been determined for the thermal decomposition of the analogous alkane, neopentane.<sup>36</sup> Such a result is not surprising since tetramethylsilane is a "looser" molecule than neopentane; the Si-C bond length in tetramethylsilane is 1.89 Å<sup>37</sup> compared to the C-C bond length in neopentane of 1.54 Å and several vibrational frequencies in tetramethylsilane are lower than those in neopentane.<sup>38</sup> Therefore, if neopentane and tetramethylsilane decompose via activated complexes having similar entropies, the entropy of activation would be larger for neopentane, resulting in a larger A factor for neopentane decomposition.

Davidson and co-workers have measured A factors between 1013 and 1013.5 sec-1 for ethylpentamethyldisilane decomposition<sup>25</sup> and between 10<sup>12.5</sup> and 10<sup>14.5</sup> sec<sup>-1</sup> for hexamethyldisilane decomposition.<sup>39</sup> They proposed that both molecules decompose by Si-Si rupture. Using the same arguments discussed above, the A factors for the decomposition of the alkyldisilanes should less than the A factor for tetramethylsilane decomposition, which is in agreement with the results of this study.

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<sup>21</sup> For example,  $\Delta H_{f288}$  (TEMS) has been calculated to be 80 kcal/mole, Ref. 17, and -26 kcal/mole, Ref. 18.

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