The Decomposition Kinetics of Chemically Activated Methyl-d₁methylsilane-d₂ and Ethylsilane-d₃*

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Abstract

The decomposition kinetics of chemically activated methyl- d_1 -methylsilane- d_2 (DMS- d_3^*) and ethylsilane- d_3 (ES- d_3) from the Si-D and C-H insertion reactions of CH₂ (1A_1) with methylsilane- d_3 have been studied. The total rate constants for decomposition of chemically activated DMS- d_3 and ES- d_3 have been measured. The individual rate constants for molecular elimination of CH_3D , CH_2D_2 , and D_2 from $DMS-d_3^*$ and for molecular elimination of CH_3CH_2D and D_2 from ES- d_3^* have been measured. All of the above rate constants exhibit the expected kinetic isotope effect when compared to those found previously in the undeuterated system. RRKM theory calculations of the rate constants for the expected C-Si and Si-D bond rupture processes, based on energetics and activated complex models deduced previously for the undeuterated system, were carried out. In the case of DMS- d_3^* the RRKM theory calculations of rate constants for the bond rupture processes combined with experimental rate constants for the molecular elimination processes gave a total rate constant for decomposition in agreement with the measured value. The results of a high-pressure study of the CH_3D/CH_2D_2 ratio from chemically activated DMS- d_3 decomposition were consistent with complete randomization of internal energy up to a pressure of 4 atmospheres (lifetime of $\sim 1.7 \times 10^{-11}$ sec). This is not an unexpected result in light of earlier work.

Introduction

The rate at which internal energy, in excess of the critical energy for decomposition, is randomized within a chemically activated molecule is of interest since predictions of decomposition rate constants via the Rice, Ramsperger, Kassel, and Marcus (RRKM) formulation are based upon the assumption that this excess energy is randomized over the normal modes of the molecule much faster than the rate of decomposition [1,2]. Tests of this assumption are significant since RRKM theory represents the most accurate and facile current theoretical method of calculating unimolecular rate constants [3].

Rynbrandt and Rabinovitch [4] have investigated decomposition rates

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of chemically activated molecules in which a "bottleneck" to rapid energy transfer was a predominant structural feature of the molecule. Chemically activated hexafluorobicyclopropyl, formed in the reaction of methylene- d_2 with hexafluorovinylcyclopropane, was observed to decompose in a fashion

$$\begin{array}{ccc} \mathbf{CF}_2 & \mathbf{CF}_2 \\ | \searrow \mathbf{CF} & -\mathbf{CF} = \mathbf{CF}_2 \\ \mathbf{CH}_2 \end{array} + \begin{array}{ccc} ^1\mathbf{CD}_2 & \rightarrow & \begin{array}{ccc} \mathbf{CF}_2 & \mathbf{CD}_2^* \\ | \searrow \mathbf{CF} & -\mathbf{CF} < | \\ \mathbf{CH}_2 & \mathbf{CF} < | \\ \mathbf{CF}_2 \end{array}$$

indicative of nonrandomization of internal energy. The characteristic decomposition reaction is elimination of CF_2 from either ring to give the two different tetrafluorovinylcyclopropane- d_2 isomers, (I) and (II):

At high pressures (short lifetimes), (I) was observed to predominate over (II) in the product mixture, indicative of CF_2 elimination being favored from the ring created in the chemical activation process.

Chemically activated methyl- d_1 -methylsilane- d_2 , CH₃SiD₂CH₂D^{*}, referred to subsequently as dimethylsilane- d_3^* , produced by the insertion of singlet methylene into a silicon-deuterium bond of methylsilane- d_3 , permits examination of the energy randomization rate in a system more typical of most molecules than hexafluorobicyclopropyl. At the time of formation, excess energy acquired by the dimethylsilane- d_3^* would be expected to reside within the "heavy" methyl portion of the molecule, that is, the CH₂D Evolution in time results in the energy being distributed moietv. throughout the molecule. The collision frequency, which is proportional to reactor pressure, provides a time base for the reaction, since under the strong collision hypothesis [5] a collision of the activated molecule with a bath gas will remove sufficient energy so as to prevent the molecule from decomposing. At sufficiently high-pressure, large collision frequency, the excess energy will be removed from the chemically activated molecule before a significant amount of energy randomization can take place. Thus the prediction is made that at sufficiently high pressures, decomposition products from the "heavy" side of the molecule will predominate over products from the "light" side. A second prediction is that as the pressure is lowered, that is, at smaller collision frequencies, there will be nearly equal yield of products from both sides of the molecule, since the slower rate of energy removal from the chemically activated molecule will permit complete randomization of the excess internal energy prior to decomposition.

The corresponding light molecule, dimethylsilane, $(CH_3)_2SiH_2$, has been intensively studied [6], as have various other silanes [7–12], via chemical

activation techniques. This information provides a basis for interpretation of the results from the dimethylsilane d_3 system. The earlier chemical activation work with dimethylsilane noted that methane and hydrogen were major products of the decomposition under reaction conditions which virtually eliminate secondary radical reaction products, among which methane, hydrogen, and higher silanes might be expected. This was accomplished by the addition of a radical scavenger, either oxygen or butadiene, to the reaction mixtures and observing that the yield of several of the higher silanes, such as methyldisilane and methylethylsilane, previously observed in unscavenged reactions [7], were greatly reduced. This result indicates that the processes of concerted molecular elimination of methane and hydrogen from chemically activated dimethylsilane are significant decomposition pathways. Dimethylsilane- d_3^* decomposition provides a unique opportunity to conclusively demonstrate that molecular elimination paths are indeed important.

In the case of complete randomization of excess energy, equal amounts of the two isotopic methanes CH_2D_2 and CH_3D should be observed, together with a significant amount of deuterium, D_2 . Observation of these three products, with rate constants for their formation consistent with the expected isotope effects relative to the light system, would constitute proof that concerted molecular eliminations do indeed occur as decomposition pathways for chemically activated dimethylsilane- d_3 .

Experimental Methods

Materials

Methylsilane- d_3 (MS) was prepared *in vacuo* by the reaction of methyltrichlorosilane (Pierce Chemical Company) and excess lithium aluminum deuteride (Stohler Isotope Chemicals) using butyl ether, previously dried in lithium aluminum hydride, as a solvent. The fraction condensed at 77°K was purified by glpc and stored at ambient temperature.

Diazomethane (DM) was prepared *in vacuo* by the reaction of sodium hydroxide on *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Matheson, Coleman, and Bell) using 1,4-butanediol as a solvent. The fraction condensed at 77°K was transferred to a dibutylphthalate solution and stored at 77°K.

Butadiene (BD) and *n*-butane (nB) were used as obtained from lecture bottles (Baker). Oxygen was commercial material, passed through a 195° K trap prior to storage for later use.

Apparatus

A conventional high-vacuum gas-handling system featuring greaseless stopcocks in the reactant measuring section was employed. Reaction vessels were of Pyrex, equipped with greaseless stopcocks only in the case of volumes less than 50 cm^3 .

Procedure

Mixtures of reactants were photolyzed at 3660 Å for various times dependent on the total pressure. The wavelength was isolated by an Esco Products filter, #5970, from a medium-pressure mercury source, Hanovia #673A36. Approximate ratios of the reactants were MS:BD:DM, 3:6:1; MS:DM:O₂, 6:1:1; MS:DM:nB:O₂, 5:1:1:1. Total pressures ranged from 0.5 to 200 cm Hg, achieved by varying reactor volume and/or total amounts of reactants.

Analysis

Following photolysis, a sample of a standard mixture of argon and nbutane was added to those reaction mixtures for which analyses of the yields of methanes or hydrogens were desired. The argon was Toepler pumped with the incondensibles (77°K) and measured mass spectrometrically. Calibration mixtures containing D₂ and argon or CH₄, CD₄, and argon were run immediately prior to and after each mass-spectrometric measurement.

The added *n*-butane was analyzed with the condensibles via glpc. A column consisting of 25 feet of 30% dibutylphthalate and 4 feet of 30% dinonylphthalate on Chromasorb, with a flow of 43 cm³/sec and an oven temperature of about 25°C, permitted analyses of *n*-butane, dimethylsilane- d_3 , ethylsilane- d_3 , and *n*-pentane. A first pass through the column removed approximately 90% of the unreacted methylsilane- d_3 , facilitating quantitative measurement of the reaction products by a second pass through the column. Authentic samples of the products, in varying proportions, approximating the various experiments, were measured for calibration of the instrument. In those experiments in which ethane was measured, the second pass was through a column consisting of 11 feet of Ascarite, 25 feet of silver nitrate, and 35 feet of 30% dinonylphthalate, all other conditions being identical. As previously, authentic samples were prepared for calibration of the instrument.

Experimental Results

Products

The principal products observed in a typical reaction were dimethylsilane- d_3 , ethylsilane- d_3 , CH₂D₂, CH₃D, D₂, and ethane- d_1 . Trace amounts of CH₄, HD, and H₂ were noted. Addition of *n*-butane for the purpose of monitoring the total CH₂ (¹A₁) reaction gave *n*-pentane and *iso*-pentane as products. The presence of a radical scavenger, butadiene or oxygen, eliminated products of triplet methylene reaction and reduced the levels of some higher silanes. These products have been detected previously in unscavenged reactions [6] and attributed to secondary reactions of silyl radicals with the methylsilane substrate [7].

The ratios of various methanes or of deuterium to dimethylsilane- d_3 were observed to decrease with increasing pressure while the ratio of dimethylsilane- d_3 to ethylsilane- d_3 approached a constant value at higher pressures. These observations are quantitatively discussed below as is the significance of the minor products, CH₄ and HD.

 H_2 formation is an artifact of the system. Experiments were performed in which diazomethane and butadiene, with and without propane addition to replace the pressure of methylsilane- d_3 , in the same proportions as in a typical experiment, were photolyzed. H_2 was observed in all cases and in the same amounts as when methylsilane- d_3 was present. From this observation it was concluded that H_2 is a reaction product formed in the photolysis of diazomethane and butadiene mixtures and consequently could be ignored. Molecular hydrogen has been reported in reactions of methylene and oxygen [13], thus accounting for the H_2 observed in the oxygen scavenged systems.

Mechanism

The following methanism, analogous to that for the light system [6], accounts for the major products and their relative pressure dependencies:

(1)
$$\operatorname{CH}_2 N_2 + h\nu \to \operatorname{Ch}_2 + N_2$$

(2)
$$CH_2 + CH_3SiD_3 \rightarrow CH_3SiD_2CH_2D^*$$
 (DMS- d_3^*)

$$(3) \qquad \rightarrow \mathrm{CH}_3\mathrm{CH}_2\mathrm{SiD}_3^* \quad (\mathrm{ES}\text{-}d_3^*)$$

$$(4) \qquad \rightarrow \dot{C}H_2D + CH_3\dot{S}iD_2$$

(5)
$$CH_3SiD_2CH_2D^* \xrightarrow{w} CH_3SiD_2CH_2D$$
 (DMS-d₃)

(6)
$$\xrightarrow{R_{\rm T}}$$
 decomposition products

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$$\rightarrow$$
 $\dot{C}H_3 + CH_2D\dot{S}iD_2$ (8) \rightarrow $\dot{C}H_2D + CH_3\dot{S}iD_2$ (9) \rightarrow $\dot{D} + CH_3\dot{S}iDCH_2D$ (10) \rightarrow $CH_3D + CH_2D\dot{S}iD$ (11) \rightarrow $CH_2D_2 + CH_3\dot{S}iD$ (12) \rightarrow $D_2 + CH_3\dot{S}iCH_2D$ (13) $CH_3CH_2SiD_3^* \xrightarrow{w} CH_3CH_2SiD_3$ (ES)(14) $\xrightarrow{k'_T}$ decomposition products(15) \rightarrow $\dot{D} + CH_3CH_2\dot{S}iD_2$ (16) \rightarrow $CH_3\dot{C}H_2 + \dot{S}iD_3$

. . . .

$$(17) \qquad \rightarrow D_2 + CH_3 CH_2 SiD$$

$$(18) \longrightarrow CH_3CH_2D + SiD_2$$

$$(19) \qquad \rightarrow \mathrm{CH}_2\mathrm{CH}_2 + \mathrm{SiHD}_3$$

(20)
$$\operatorname{CH}_2 + n \cdot \operatorname{C}_4 \operatorname{H}_{1-} \rightarrow n \cdot \operatorname{C}_5 \operatorname{H}_{12}^* \xrightarrow{w} n \cdot \operatorname{C}_5 \operatorname{H}_{12} \quad (n \operatorname{P})$$

(21)
$$\rightarrow iso-C_5H_{12}^* \xrightarrow{\omega} iso-C_5H_{12}$$

In this mechanism an asterisk denotes a molecule whose internal rotational plus vibrational energy is in excess of that required for decomposition, w denotes the collision frequency which is proportional to pressure. The various doublet radicals, indicated by single dots, would undoubtedly contribute to the reaction products by means of secondary reactions if the system were not suitably scavenged. The singlet silylene radicals indicated by the double dots do not appear to be efficiently scavenged by oxygen or butadiene [6], the insertion of these singlet species into silicon-deuterium bonds [14] is probably responsible for the trace amounts of the higher silanes detected. These did not interfere with the analysis for the major products and were not quantitatively determined.

Both singlet and triplet methylenes are produced in step (1). Scavenging of triplets by oxygen or butadiene eliminates step (4). The insertion reactions, steps (2) and (3), involve only the singlet species. Steps (5) through (19) describe the fate of the chemically activated molecules produced in steps (2) and (3). Steps (5) and (13) represent collisional stabilization of these energetic species in terms of the strong collision hypothesis, while step (6) for DMS- d_3^* and step (14) for ES- d_3^* count all possible decomposition pathways. The decomposition paths believed to be of major importance are indicated by steps (7) through (12) for DMS- d_3^* and steps (15) through (19) for ES- d_3^* . Steps (10) through (12) and steps (17) and (18) are proposed to proceed through molecular elimination.

Steps (20) and (21) represent the reactions when the internal standard method of determining total rate constants is used. Previous work [15] has shown that there is complete collisional stabilization of the activated pentanes, formed by the insertion of methylene into the carbon-hydrogen bonds of n-butane, at even the lowest pressures of this investigation. The collision diameters used to convert pressures to collision frequencies are the same as in the light system [6].

Total Rate Constants

Application of the steady-state approximation to DMS- d_3^* [steps (2), (5), (6), and (20)] gives the following expression for the total rate constant $k_{\rm T}$, for the decomposition of chemically activated dimethylsilane- d_3 .

(A)
$$\frac{(nP)(MS)}{(nB)(DMS)} = \frac{k_{20}k_T}{k_{2w}} + \frac{k_{20}}{k_2}$$

The experimentally measured quantity on the left-hand side of this equation is plotted against the reciprocal of the collision frequency in Figure 1. From the ratio of the slope to the intercept, a value for the total decomposition rate constant of the chemically activated dimethylsilane- d_3 was obtained and is entered in Table I.

A similar expression may be derived for the total rate constant $k'_{\rm T}$ for chemically activated ethylsilane- d_3 decomposition by application of the steady-state approximation [steps (3), (13), (14), and (20)]. The ratio of this expression to eq. (A) yields eq. (B):



Figure 1. Internal standard method for dimethylsilane- d_3 . The total decomposition rate constant $k_{\rm T}$ is given by the ratio of the slope to the intercept. $k_{\rm T} = (1.76 \pm 0.23) \times 10^9 \, {\rm sec^{-1}}$.

Process	<u>k/(1</u>	$10^9 \mathrm{sec}^{-1})$
	this stud	ly light system ^a
""	1.76 ± 0.	23 4.0
k ₇	[0.307 ± 0.	023] ^{<u>b</u>}
^k 8	[0.308 ± 0.	023] <u>b</u>
k ₉	$[0.091 \pm 0.$	$006]^{\underline{b}}$ 0.30
^k 10	0.282 ± 0.	0.85
k _{ll}	0.254 ± 0.	.007
^k 12	0.75 ^C	1.90
k'T	3.23 ± 0.	60 8.5
k ₁₅	$[0.054 \pm 0.$.003] ^{<u>b</u>} 0.14
k ₁₆	[0.531 ± 0.	.030] ^{<u>b</u>} 0.78
^k 17	0.75 ^C	1.9
^k 18	0.434 ± 0.	.024 1.4
^k 19	1.5 <u>d</u>	4.3

TABLE I. Experimental and calculated rate constants.

^a From [6].

^b Average of RRKM calculations. Models fitted to light system.

^c Deduced, see text. This is a maximum for k_{12} , a minimum for k_{17} .

^d Deduced by difference: $k_{19} = k'_{T} - k_{16} - k_{17} - k_{18}$.

(B)
$$\frac{\text{(DMS)}}{\text{(ES)}} = \frac{k_2}{k_3} \frac{(k_{\rm T}' + w)}{(k_{\rm T} + w)}$$

Equation (B) can be used to investigate the pressure dependence of the relative yields of the two stabilized molecules as well as to deduce the initial relative populations of the two excited molecules.

Expansion of eq. (B) by means of the binomial theorem gives, keeping first-order terms only,

(C)
$$\frac{(DMS)}{(ES)} = \frac{k_2}{k_3} \frac{k'_T}{k_T} + wA, \quad w < k_T$$

and

(D)
$$\frac{(\text{DMS})}{(\text{ES})} = \frac{k_2}{k_3} + \frac{1}{w}B, \quad w > k_T$$

where A and B are collections of rate constants and have no special significance. The experimental data were divided at $w = 1.76 \times 10^9 \text{ sec}^{-1} = k_{\text{T}}$. The data were plotted according to eqs. (C) and (D), and least-square intercepts were evaluated for the two sets of data.

The intercept of the data plotted according eq. (D) gives a value of k_2/k_3

= 7.4 ± 0.6 . This is in good agreement with the value of 7.7 ± 0.3 reported by Mazac and Simons [8] in a previous high-pressure investigation of this system.

The intercept of eq. (C) gives $k_2 k'_T / k_3 k_T = 13.6 \pm 1.1$ from which a value of $k'_T = (3.23 \pm 0.60) \times 10^9 \text{ sec}^{-1}$ is obtained using the values of k_T and k_2 / k_3 deduced above. This value of k'_T is entered in Table I.

Decomposition of Dimethylsilane- d_3

Step (6) is proposed to consist of the sum of reactions (7) through (12) which represent decomposition of the chemically activated molecule into radicals by rupture of the various silicon–carbon and silicon–deuterium bonds as well as molecular elimination of methane and deuterium. The three indicated radical decomposition pathways are considered later via RRKM theory. The formation of CH₃D, CH₂D₂, and D₂, steps (10), (11), and (12), is believed to proceed by three centered molecular eliminations, that is, simultaneous rutpure of two bonds to silicon and formation of a new bond between the two fragments.

Application of the steady-state hypothesis to steps (5) and (10) or (11) gives eq. (E):

(E)
$$\frac{D_i}{S} = \frac{k_i}{w}$$

 D_i is either of the decomposition products, CH_3D or CH_2D_2 , and S is dimethylsilane- d_3 , the product of the stabilization process. The rate constant for formation of the decomposition product of interest is k_i . Data corresponding to steps (10) and (11) are plotted in Figures 2 and 3 according to eq. (E). Rate constants were calculated from the slopes and are entered



Figure 2. Relative yields of CH_3D and dimethylsilane- d_3 as a function of reciprocal collision frequency. The solid points are averages of several experiments. Three low-pressure points are not plotted so as to avoid excessive compression of the abscissa.



Figure 3. Relative yields of CH_2D_2 and dimethylsilane- d_3 as a function of reciprocal collision frequency. The solid points are averages of several experiments. Three low-pressure points are omitted so as to avoid excessive compression of the abscissa.

in Table I. It should be noted that the intercepts of Figures 2 and 3 are virtually zero. This indicates that no pressure-independent reaction pathways are producing either CH_3D or CH_2D_2 , for example, abstraction reactions of methyl radicals.

In order to determine the rate constants for deuterium production, it is noted that this molecule is the product of both reactions (12) and (17); consequently, a simple expression such as eq. (E) does not apply. Application of the steady-state approximation to (DMS^{*}) and (ES^{*}) in the rate expression for deuterium production gives eq. (F):

(F)
$$\frac{(D_2)}{(DMS)} = \frac{1}{w} k_{12} + k_{17} \frac{(ES)}{(DMS)}$$

Expanding the ratio of (ES)/(DMS) according to the binomial theorem in the region $w < k'_{\rm T}$ and keeping first-order terms only, permits eq. (F) to be rewritten as

(G)
$$\frac{(D_2)}{(DMS)} = \frac{1}{w} \left(k_{12} + \frac{k_3 k_T}{k_2 k_T} k_{17} \right) + k_{17} C$$

where C is a collection of rate constants. The experimental data are plotted in Figure 4 according eq. (G). A least-square analysis of the data gives a value of $8.1 \times 10^9 \text{ sec}^{-1}$ for the slope, $k_{12} + 0.074 k_{17}$. The intercept was ignored since the combined uncertainty of the various rate constants used to evaluate C would give a very unreliable value of k_{17} .

Since chemically activated ethylsilane- d_3 is observed to decompose faster than chemically activated dimethylsilane- d_3 , $k'_T > k_T$, it is reasonable to expect k_{12} to be no greater than k_{17} . If these two rate constants are taken as equal, a value of $7.5 \times 10^8 \text{ sec}^{-1}$ is estimated as a maximum value of k_{12} and as a minimum value of k_{17} .

A pathway in which ethane- d_1 was a molecular elimination product from



Figure 4. Relative yields of D_2 and dimethylsilane- d_3 as a function of reciprocal collision frequency. Five low-pressure points are not plotted so as to avoid excessive compression of the abscissa.

dimethylsilane- d_3 was not considered since in studies of tetraalkylsilane decompositions [15] there has been no indication of such a process. The observed ethane- d_1 is attributed to the chemically activated ethylsilane- d_3 decomposition and discussed in the next section.

Decomposition of Ethylsilane-d₃

Reaction (14) for the total rate constant for the decomposition of chemically activated ethylsilane- d_3 is proposed to consist of five contributors, steps (15)–(19). The bond rupture processes, steps (15) and (16), for the production of ethyl radicals and deuterium atoms are considered later via RRKM calculations. Reaction (18) for the production of ethane- d_1 is postulated to proceed via a three-centered molecular elimination process in a fashion similar to that for dimethylsilane- d_3 . An expression analogous to eq. (E) may be derived from steps (14) and (18). Data are plotted in Figure 5 according to this expression. A least-square analysis yields an intercept of virtually zero, indicating no parallel radical processes producing ethane. The rate constants derived from the slope of Figure 5 have been entered in Table I.

The D_2 produced via step (17) has been considered above. The final reaction, step (19), is postulated as the most likely reaction to make up the total rate constant for the decomposition of chemically activated ethylsilane- d_3 . Investigation of this reaction and experimental confirmation of the rate constant is not feasible since ethene is produced in reactions between methylenes [16]. Decomposition via c-c bond rupture would be too slow to be an important path in ethylsilane decomposition [15].



Figure 5. Relative yields of CH_3CH_2D and $ethylsilane-d_3$ as a function of reciprocal collision frequency.

Discussion

Molecular Elimination

Since the pressure dependence of CH_3D and CH_2D_2 formation did not show any evidence for abstraction reactions producing these same products, and since no other isotopic methanes were observed in the scavenged systems, the hypothesis that CH_3D and CH_2D_2 are formed by a molecular elimination mechanism is proven. The kinetic isotope effects exhibited by these two rate constants with respect to the rate constant for methane production in dimethylsilane are consistent with a three-centered molecular elimination complex. Complex structures (III) and (IV) for DMS- d_3^* and (V) for DMS* are proposed for these processes in which a deuterium or a hydrogen attached to the silicon forms a three-membered ring with the silicon and one methyl group:



The mixed primary and secondary kinetic isotope effect due to deuterium for hydrogen substitution is illustrated by comparing (III) and (IV) with (V). Referring to Table I, it is noted that the sum of k_{10} and k_{11} , constituting the total rate constant for methane production from dimethylsilane- d_3 , from dimethylsilane- d_3 , is less by a factor of 1.6 than the rate constant for methane production from dimethylsilane, in qualitative agreement with the expected kinetic isotope effect.

Hennis and coworkers have reported [17] that such a three-centered elimination from silicon is favored at least tenfold over a similar threecentered elimination from carbon. The HD observed as a minor product in our investigation can be interpreted as a three-centered elimination occurring at the methylene carbon as diagramed in structure (VI):



A very weak correlation of the measured HD/dimethylsilane- d_3 ratio indicates that the rate constant for this process is no greater than 10% of the rate constant for D₂ production which can be formed in a three-center process at the silicon, illustrated by structure (VII):



Three-center molecular elimination processes at the silicon also account for the formation of ethane- d_1 and D_2 from chemically activated ethylsilane- d_3 . These are illustrated as structures (VIII) and (IX).



It is noted that this interpretation accounts for the kinetic isotope effect observed in comparing the results of this investigation with those from the light system [6]. As in the dimethylsilane case this is a mixed primary and secondary isotope effect due to the substitution of deuterium for hydrogen in the three-member ring.

The remaining apparently minor product CH_4 is most likely not observed, but is in fact an artifact of the calculational procedure used to determine the yields of CH_2D_2 and CH_3D from the mass-spectral data. A small difference in the m/e = 16 peak height observed and that calculated from cracking of CH_3D and CH_2D_2 could indeed be a small calculational artifact.

Energy Randomization

Intramolecular energy randomization may be investigated by examining the relative yields of CH_3D and CH_2D_2 at high pressures. In Figure 6 the ratio of the measured quantities of CH_3D and CH_2D_2 is plotted as a function of reciprocal collision frequency. It will be noted that over the range of experimental data the ratio is reasonably constant, this being a good approximation to the ratio of the rate constants for the production of the two methanes k_{10} and k_{11} . The scatter in the data at higher pressures is due to the small amounts of the decomposition products, CH_3D and CH_2D_2 , and the resultant uncertainty in their measurement. Since there is no observed tendency of the ratio to change with increasing pressure (decreasing reciprocal collision frequencies), it may be concluded that virtually complete randomization of excess internal energy occurs at all pressures attained in this investigation. The highest pressure achieved corresponds to a collision frequency of $6 \times 10^{10} \text{ sec}^{-1}$. An approximate expression for $w_{\rm t}$, the collision frequency at which a detectable change in the apparent decomposition rate occurs due to nonrandomized decomposition, has been given by Rabinovitch and co-workers [4]. Taking 20% change to be a detectable change in the apparent rate yields the expression $w_{\rm t} = k_{\rm RD} \lambda / k_{\rm ND}$, where $k_{\rm RD}$ is the specific rate for randomized decomposition, $k_{\rm ND}$ the specific rate for nonrandomized decomposition, and λ the specific rate of intramolecular energy randomization. Since no change in specific rate was detected from our results up to $w = 6 \times 10^{10} \text{ sec}^{-1}$, we conclude that $w_t > 10^{10} \text{ sec}^{-1}$ $6 \times 10^{10} \text{ sec}^{-1}$. Taking $\lambda = 1 \times 10^{12} \text{ sec}^{-1}$ from [4], the above result yields $k_{\rm ND}/k_{\rm RD} < 17$. This value is about an order of magnitude too small by comparison to the relative of methane elimination from chemically activated dimethylsilane and trimethylsilane formed from Si-H insertion of $CH_2(^1A_1)$ [6,12]. This discrepancy suggests either that the formation reaction coordinate is strongly coupled to essentially all of the internal modes of the molecule or that a larger value of λ may be more appropriate for the present system.



Figure 6. Relative yields of CH_3D and CH_2D_2 as a function of reciprocal collision frequency.

RRKM Calculations

Description of the Method

Rice Ramsperger, Kassel, and Marcus (RRKM) theory [18] permits an accurate calculation of the rate constant k_E for a generalized unimolecular decomposition reaction at a specified energy E^* , residing in the energized molecule A^* . In addition to the reaction path, a knowledge of the critical energy E_0 , for decomposition and a structure for the activated complex which gives the correct entropy of activation as derived from the high-pressure thermal Arrhenius A factor are required. The value of E^* is deduced from the thermochemistry of the process producing the activated molecule.

Functionally, the rate constant is given by

$$k_{E} = \frac{d\sum_{E_{vr}^{+}=0}^{E^{+}} P(E_{vr}^{+})}{hN(E_{vr}^{*})}$$

where $k_{\rm E}$ is the specific rate constant for decomposition of the chemically activated molecule at energy E^* , d is the reaction path degeneracy, and his Planck's constant. The factor $N(E_{vr}^*)$ is the density of vibrational-active rotational states of the molecule at the energy E^* , while the factor $\Sigma P(E_{vr}^+)$ is the sum of vibrational-active rotational states for the activated complex up to energy E^+ . The subscript vr serves to emphasize the dependence of the sums and densities of states on both vibrational and active rotational states.

The Waage and Rabinovitch treatment of adiabatic rotations [19] yields eq. (I) for the relationship between E^* and E^+ :

(I)
$$E^+ = E^* - E_0 + \langle E_J^* \rangle - \langle E_J^+ \rangle$$

where $\langle E_{\rm J}^* \rangle - \langle E_{\rm J}^+ \rangle$ is the difference of the average thermal energies in the adiabatic rotations of the molecule and the complex. This term is approximated by the relationship

(J)
$$\langle E_J^* \rangle - \langle E_J^+ \rangle = \left(\left[\frac{I_x^+ I_y^+ I_z^+}{I_x I_y I_z} \right]^{1/2} - 1 \right) RT$$

where I^+ and I are the principal moments of inertia of the complex and molecule, respectively. The sum of states of the complex and the density of states of the molecule were calculated by the Whitten, Rabinovitch, and Tardy approximation [20] which is accurate at the energies of interest.

Structural Parameters and Previous Work

Normal mode analyses are available for dimethylsilane [21], ethylsilane [22], and ethylsilane- d_3 [22]. These are presented in Tables II and III. Application of the Teller-Redlich product rule [23] to the dimethylsilane frequencies yielded the frequencies in Table II for dimethylsilane- d_3 as used in this investigation.

The principal moments of inertia for the overall rotations were calculated assuming all bond angles as tetrahedral and using atomic masses and bond

Assignment	Dimethyls	ilane ^b	Dimethylsi	lane-d ₃ ^c
C-H stretch	2967	(4)	2967	(3)
	2899	(2)	2100	
			2899	(2)
Si-C stretch	724	<u>d</u>	724	
	655		655	
Si-H stretch	2132	<u>e</u>	1505	
	2138		1510	
CH ₃ rock	882		882	
	868		868	
	857	<u>d</u>	857	
	841	d	841	
C-Si-C bend	227	<u>d</u>	227	
CH ₃ deformation	1267	(2)	1267	
	1433	(4)	958	
			1087	
			1433	(3)
SiH ₂ twist	760	<u>e</u>	575	
wag	915	e	693	
rock	469	<u>d,e</u>	355	
sissors	949	<u>e</u>	718	
Internal Rotor	FR	(2)	FR	(2)

TABLE II. Vibrational assignments of dimethylsilanes.^a

^a Units are cm⁻¹.

^b From [21].

^c Deduced from application of the Teller-Redlich product rule.

^d Frequencies lowered in methyl rupture complex.

^e Frequencies lowered in hydrogen rutpure complex.

Assignment	Ethylsilane	Ethylsilane-d3
Methyl C-H stretch	2963	2963
	2891	2891
	2970	2970
Methyl H-C-H bends	1465 (2)	1465 (2)
	1411	1411
C-C stretch	1021	1021
Methylene C-H stretch	2932	2932
	2978	2978
CH ₃ -C rock	973 (2)	973 (2)
CH ₂ scissors	1411	1411
wag	1239	1239
twist	1239	1239
rock	764	<u>b</u> 724
SiH ₃ -C rock	602	<u>b</u> 492
	515	<u>b</u> 419
C-Si stretch	699	<u>b</u> 639
H-Si-H bends	937 (3)	<u>c</u> 711 (3)
H-Si stretch	2164 (3)	<u>c</u> 1568 (3)
C-C-Si bend ^{<u>d</u>}	300	<u>b</u> 300
Internal rotor	FR (2)	FR (2)

TABLE III. Vibrational assignments of ethylsilanes.^a

^a From [22].

^b Frequencies lowered in the ethyl rupture complex.

^c Frequencies lowered in the hydrogen rupture complex.

^d Estimated value.

lengths available in the literature [24]. Since the moments of inertia enter into the RRKM calculation as a ratio of complex to molecule values, inaccuracies due to delection of bond angles and bond lengths are minimized.

Haze, Mazac, and Simons [6] have suggested three possible activated complex models for methyl rupture from dimethylsilane. The models are presented in Table IV together with calculated rate constants. The ratio of the product of the principal moments of inertia for the adiabatic rotations of the complex to the molecules was taken to be 2.56, which corresponds

Molecule	Methyl	Rupture	Complex ^b	Si-H	Rupture	Complex ^C
Frequencies	1	11	111	1	11	111
2132				RC	RC	RC
949				376	226	128
915				363	218	124
857	371	244	152			
841	367	239	149			
760				301	182	102
724	RC	RC	RC			
469	205	133	84	187	113	63
227	99	65	40			
Eod	74	78	82	81	85	89
E*d	133	129	125	133	129	125
log A/path ^e	14.92	15.65	16.47	15.26	16.14	17.13
$k_E \times 10^{-9} \frac{f}{-1}$	0.933	0.938	0.945	0.302	0.300	0.303
I ⁺ _x I ⁺ _y I ⁺ _z /I _x I _y I _z		2.56			1.05	

TABLE IV. Bond rupture decomposition of CH₃SiH₂CH^{*}₃.^a

^{*a*} Units are cm^{-1} ; - - means unchanged from molecule.

^b The complex is altered slightly from published model [6] in order to better fit experimental k_7 for the "light" system [6]. These frequencies are lowered relative to the molecule by factors of 2.30, 3.51, and 5.64 for models I, II, and III, respectively, giving "tightest," "best," and "loosest" models consistent with uncertainty ranges in E_0 and E^* .

^c These frequencies are lowered relative to the molecule by factors of 2.52, 4.18, and 7.42 for models I, II, and III, respectively.

^d Units are kcal/mol.

^e Calculated at 1000°K by activated complex theory [25].

^f Units are sec⁻¹.

to a Si–C bond of the complex lengthened by a factor of 1.43, from 1.86 to 2.66 Å. This extension is taken as a characteristic of the Si–C bond rupture process for $\dot{C}H_3$ and $\dot{C}H_2D$ from dimethylsilane- d_3 and $CH_3\dot{C}H_2$ from ethylsilane and ethylsilane- d_3 . Rupture of the Si–D or Si–H bond from both dimethylsilanes and both ethylsilanes was considered to proceed through an activated complex in which the Si–D or Si–H bond was lengthened by a factor of 1.5, from 1.48 to 2.22 Å.

Energetics

The critical energy E_0 for the bond rupture processes of silanes is given by the bond dissociation energy, there being virtually zero activation energy for the radical recombination process [26]. In the case of methyl rupture from silicon, the value of 78 ± 4 kcal/mol used in the earlier calculations on the light system [6] represents an average value of electron impact and thermal activation energy measurements [27]. This value was used unchanged for both methyl rupture processes from dimethylsilane- d_3 since any secondary isotope effect on this energy would be within the large uncertainty indicated.

In the case of hydrogen rupture from silicon, 85 ± 4 kcal/mol represents an average value of the reported results of the Si-H bond dissociation energy [27a,28], the range resulting in part from a variety of alkyl substituents on the silicon. This value was used for hydrogen rupture from silicon in both ethylsilane and dimethylsilane. Results from recoil tritium experiments [29] indicate that the bond dissociation energy of the Si-D bond of trimethylsilane- d_1 is approximately 2 kcal/mol greater than for the corresponding undeuterated molecule. Using this value, the critical energy for Si-D bond rupture from dimethylsilane- d_3 and ethylsilane- d_3 becomes 87 ± 4 kcal/mol.

The Si-CH₂CH₃ bond dissociation energy is about 3 kcal/mol less than the corresponding Si-CH₃ bond dissociation energy [10]. This indicates that the critical energy for ethyl rupture from ethylsilane and ethylsilane- d_3 is 75 ± 4 kcal/mol, again assuming a negligible secondary isotope effect on E_0 .

The average energy E^* of the chemically activated dimethylsilane- d_3 is given by

(K)
$$E^* = \Delta H^{\circ}_{f0}(CH_3SiD_3) - \Delta H^{\circ}_{f0}(CH_3SiD_2CH_2D) + [\Delta H^{\circ}_{f0}({}^{1}CH_2) + E^*({}^{1}CH_2)] + E_{TH}$$

where E_{TH} is the average thermal vibrational-internal rotational energy of the formed excited molecule as calculated via statistical mechanics and has a value of 2.6 kcal/mol for the light system and 2.8 kcal/mol for the heavy. The expression for E^* of chemically activated ethylsilane- d_3 follows by substitution of $\Delta H_{f0}^{\circ}(\text{CH}_3\text{CH}_2\text{SiD}_3)$ for the second term of the right-hand side of eq. (K). The methylene energy $[\Delta H_{f0}^{\circ}(^1\text{CH}_2) + E^*(^1\text{CH}_2)]$, has been determined [30] to be 116.1 kcal/mol for diazomethane photolysis at 3660 Å.

The difference in heats of formation of methylsilane- d_3 and dimethylsilane- d_3 is given by

(L)
$$\Delta H_{f0}^{\circ}(CH_3SiD_3) - \Delta H_{f0}^{\circ}(CH_3SiD_2CH_2D) = D_{298}^{\circ}(CH_3SiD_2-CH_2D) - D_{298}^{\circ}(CH_3SiD_2-D) + \Delta H_{f\,298}^{\circ}(D) - \Delta H_{f\,289}^{\circ}(CH_2D) - \Delta H_{CORR}$$

where ΔH_{CORR} corrects values at 298° to 0°K. The expression for light

dimethylsilane equivalent to eq. (L) has been evaluated [6] to be 10.5 ± 4 kcal/mol. Based on the bond dissociation energies deduced previously, a value of 10.2 ± 4 kcal/mol results for the heavy system using $\Delta H_{f\,298}^{\circ}(D) = 53$ kcal/mol and estimating $\Delta H_{f\,298}^{\circ}(CH_2D)$ as 35 kcal/mol. The corresponding quantities of the light system, $\Delta H_{f\,298}^{\circ}(H)$ and $\Delta H_{f\,298}^{\circ}(CH_3)$, are 52 kcal/mol and 34 kcal/mol, respectively. The change in ΔH_{CORR} from the light system to the heavy is expected to be identical to the change in E_{TH} .

The expression equivalent to eq. (L) for the ethylsilane system was evaluted [10] to be 3.5 ± 0.5 kcal/mol. Since deuterium substitution is not directly involved in this thermochemistry, this value was used unchanged for the heavy system.

Combining the values for the differences in heats of formation with the value for the methylene energy gives the average energy E^* of dimethylsilane- d_3 and both ethylsilane and ethylsilane- d_3 . The value of E^* used for the calculations on dimethylsilane was the value from the previous investigation [6].

In the Whitten, Rabinovitch, and Tardy approximation for the sums of states of the activated complex and the density of states of the molecule, the partition functions for internal rotations enter as multiplicative factors. Since there is no change in the number of internal rotors between complex and molecule, only the ratio of the square roots of the reduced rotational moments enters into the calculation, the free rotor model being assumed in view of the small barrier potentials for these molecules [32]. This ratio was taken as one for calculating the specific rate constants. The exact reduced rotational moments [32] were used to calculate the Arrhenius A factors [25] which incorporate the entropies of activation for the formation of the complex.

New Calculations

After the fashion of Hase, Mazac, and Simons [6] three complex models were derived for each process of the light system—hydrogen rupture from both dimethylsilane and ethylsilane and ethyl rupture from ethylsilane. The entropies of activation of these models were so selected that when combined with the energetics in the usual fashion, high activation entropy with low critical energy, etc., the rate constants predicted previously [6] were reproduced as accurately as possible by each model. As noted for the methyl rupture process from dimethylsilane, these models represent the "tightest," best," and "loosest" complexes consistent with the range of permissible energies.

Activated complex models for the deuterated systems were constructed by substituting the frequencies altered by deuterium replacement in the molecule, then lowering those frequencies altered in complex formation by the same factor as for the undeuterated systems. In a similar fashion, principal moments of inertia and energetics for the deuterated systems were substituted for those of the undeuterated systems. As a verification of this procedure for deducing the activated complexes for the deuterated systems, the Teller–Redlich product rule was applied to the deuterated and undeuterated activated complex pairs for each model of each bond rupture process. The complexes for rupture of a carbon–silicon bond, methyl from a dimethylsilane and ethyl from an ethylsilane, obeyed the product rule. The complexes for rupture of a hydrogen–silicon versus a deuterium–silicon bond in dimethylsilane and in ethylsilane gave moderate agreement to the product rule.

The results of these calculations are summarized in Tables IV–VII. The averages of the specific rate constants calculated for the three models for each bond rupture process have been entered in Table I.

Molecule Frequencies	Ethyl Ru I	ipture (II	Complex ^b III		Si-H R I	Rupture (II	Complex ^C III
2164					RC	RC	RC
2164(2)				1	907(2)	536(2)	289(2)
937(3)					393(3)	232(3)	125(3)
764	291	188	116				
619	RC	RC	RC				
602	230	149	91				
515	197	128	77				
300	114	74	45				
Eod	71	75	79		81	85	89
E*	126	122	118		126	122	118
log A/path ^e	15.17	15.39	16.78		15.33	16.42	17.74
$k_E \times 10^{-9} \frac{f}{-1}$	0.784	0.769	0.770	(0.143	0.134	0.139
I ⁺ _x I ⁺ _y I ⁺ _z /I _x I _y I _z		2.80				1.12	

TABLE V. Bond rupture decomposition of CH₃CH₂SiH^{*}₃.^a

^{*a*} Units are cm^{-1} ; - - means unchanged from molecule.

^b These frequencies are lowered relative to the molecule by factors of 2.62, 4.05, and 6.64 for models I, II, and III, respectively.

 $^{\rm c}$ The frequencies are lowered relative to the molecule by factors of 2.38, 4.04, and 7.49 for models I, II, and III, respectively.

^d Units are kcal/mol.

" Calculated at 1000°K by activated complex theory [25].

/ Units are sec⁻¹.

Molecule Frequencies	Methyl I	Rupture II	Complex ^b III	Si-D I	Rupture II	Complex ^C III
1505				RC	RC	RC
857	372	244	152			
841	366	240	149			
724	RC	RC	RC			
718				285	172	97
693				275	166	93
575				228	138	77
355	154	101	63	141	85	48
227	99	65	40			
$E_o^{\frac{d}{d}}$	74	78	82	83	87	91
Etd	133	129	125	133	129	125
log A/path	14.92	15.65	16.47	15.23	16.10	17.10
$k_E \times 10^{-9} \frac{f}{-1}$	0.662	0,613	0.571	0.874	0.877	0.875
I ⁺ _x I ⁺ _y I ⁺ _z /I _x I _y I _z		2.49			1.15	

TABLE VI. Bond rupture decomposition of CH₃SiD₂CH₂D*.^a

^{*a*} Units are cm⁻¹; - - means unchanged from molecule.

 b These frequencies are lowered relative to the molecule by factors of 2.30, 3.51, and 5.64 for models I, II, and III, respectively.

 $^{\rm c}$ These frequencies are lowered relative to the molecule by factors of 2.52, 4.18, and 7.42 for models I, II, and III, respectively.

^d Units are kcal/mol.

^e Calculate at 1000°K by activated complex theory [25].

^{*f*} Units are sec⁻¹.

Conclusions

(a) An examination of the results in Table I demonstrates that the activated complexes designed to fit, via RRKM theory, the estimated rate constants for the bond rupture processes of chemically activated dimethylsilane and ethylsilane, utilizing the best available energetics, adequately fit the results for the corresponding processes of chemical activated dimethylsilane- d_3 and ethylsilane- d_3 if the appropriate vibrational frequency and energy changes required by the isotopic substitutions are made.

(b) The isotopic composition of the methanes, primarily CH_2D_2 and CH_3D , and of the hydrogens, primarily D_2 , clearly demonstrate that mo-

Molecule Frequencies	Ethyl F I	Rupture II	Complex ^b III	Si-D I	Rupture (II	Complex ^C III
1568				RC	RC	RC
1568(2)				659	(2) 388(2)	209(2)
724	276	179	109			
711(3)				299	(3) 176(3)	95(3)
639	RC	RC	RC			
492	188	121	74			
419	160	103	63			
300	114	74	45			
E_{o}^{d}	71	75	79	83	87	91
E*d	126	122	118	126	122	118
log A/path ^e	15.20	15.97	16.82	15.38	3 16.51	17.83
$k_{E} \times 10^{-9} \frac{f}{-1}$	0.561	0.531	0.501	0.0572	2 00537	0.0514
I ⁺ _x I ⁺ _y I ⁺ _z /I _x I _y I _z		3.53			1.21	

TABLE VII. Bond rupture decomposition of CH₃CH₂SiD₃^{*}.^a

^{*a*} Units are cm^{-1} ; - - means unchanged from molecule.

^b These frequencies are lowered relative to the molecule by factors of 2.62, 4.05, and 6.64 for models I, II, and III, respectively.

^c These frequencies are lowered relative to the molecule by factors of 2.38, 4.04, and 7.49 for models I, II, and III, respectively.

^d Units are kcal/mol.

^e Calculated at 1000°K by activated complex theory [25].

^f Units are sec⁻¹.

lecular decomposition paths lead to these products.

(c) The pressure independence of the ratio CH_3D/CH_2D , up to a pressure of 4 atmospheres, suggests rapid intramolecular energy randomization in chemically activated $CH_3SiD_2CH_2D$ formed from $CH_2(^1A_1) + CH_3SiD_3$.

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Bibliography

- [1] B. S. Rabinovitch and M. C. Flowers, Q. Rev., 18, 122 (1964).
- [2] B. S. Rabinovitch and D. W. Setser, Adv. Photochem., 3, 1 (1964).
- [3] P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley Interscience, New York, 1972, p. 64.
- [4] J. D. Rynbrandt and B. S. Rabinovitch, J. Phys. Chem., 75, 2164 (1971); J. F. Meagher,
 K. J. Chao, J. R. Barker, and B. S. Rabinovitch, *ibid.*, 78, 2535 (1974).
- [5] G. H. Kohlmaier and B. S. Rabinovitch, J. Chem. Phys., 38, 1692 (1963).
- [6] W. L. Hase, C. J. Bazac, and J. W. Simons, J. Am. Chem. Soc., 95, 3454 (1973).
- [7] J. W. Simons and C. J. Mazac, Can. J. Chem., 45, 1717 (1967).
- [8] C. J. Mazac and J. W. Simons, J. Am. Chem. Soc., 90, 2484 (1968).
- [9] W. L. Hase and J. W. Simons, J. Chem. Phys., 52, 4004 (1970).
- [10] W. L. Hase and J. W. Simons, J. Organomet. Chem., 32, 47 (1971).
- [11] W. L. Hase, W. G. Brieland, and J. W. Simons, J. Phys. Chem., 75, 4001 (1969).
- [12] W. L. Hase, W. G. Brieland, P. W. McGrath, and J. W. Simons, J. Phys. Chem., 76, 459 (1972).
- [13] R. L. Russel and F. S. Rowland, J. Am. Chem. Soc., 90, 1671 (1968).
- [14] B. Cox and H. Durnell, J. Chem. Soc. Faraday Trans. I, 71, 859 (1975).
- [15] W. L. Hase, R. L. Johnson, and J. W. Simons, Int. J. Chem. Kinet., 4, 1 (1972); F. B. Growcock, W. L. Hase, and J. W. Simons, J. Phys. Chem., 76, 607 (1972); and references cited therein.
- [16] H. M. Frey, Prog. React. Kinet., 2, 131 (1964).
- [17] (a) J. M. S. Hennis, G. W. Stewart, and P. P. Gaspar, J. Chem. Phys., 61, 4860 (1974);
 (b) J. M. S. Hennis and M. K, Tripodi, *ibid.*, 61, 4863 (1974).
- [18] (a) R. A. Marcus, J. Chem. Phys., 20, 352 (1952); (b) R. A. Marcus, *ibid.*, 43, 2658 (1865);
 (c) R. A. Marcus and G. K. Rice, J. Phys. Colloid Chem., 55, 894 (1951); (d) G. V. Waage and B. S. Rabinovitch, Chem. Rev., 70, 377 (1970).
- [19] G. V. Waage and B. S. Rabinovitch, J. Chem. Phys., 52, 5581 (1970).
- [20] (a) G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys., 38, 2466 (1963); (b) G. Z.
 Whitten and B. S. Rabinovitch, *ibid.*, 41, 1883 (1964); (c) D. C. Tardy, B. S. Rabinovitch, and G. Z. Whitten, *ibid.*, 48, 1427 (1968).
- [21] J. F. Kolalev, Opt. Spectrosc. (USSR), 8, 166 (1960).
- [22] K. M. Mackay and R. Watt, Spectrochim. Acta, 23A, 2761 (1967).
- [23] G. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955, p. 183.
- [24] (a) M. T. Tribble and N. L. Allinger, Tetrahedron, 28, 2147 (1972);
 (b) G. R. Wilkinson and M. K. Wilson, J. Chem. Phys., 44, 3867 (1965).
- [25] S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 181.
- [26] (a) H. Shaw and S. Toby, J. Phys. Chem., 72, 2337 (1968); (b) A. Shepp, J. Chem. Phys., 24, 939 (1956); (c) A. Shepp and K. O. Kutschke, *ibid.*, 26, 1020 (1957); (d) J. C. J. Thyne, J. Organometal. Chem., 17, 155 (1969); (e) L. C. Glasgow, O. Olbrich, and D. Potzinger, Chem. Phys. Lett., 14, 466 (1972).
- [27] (a) M. F. Lappert, J. Simpson, and T. R. Spaulding, J. Organomet. Chem., 17, P1 (1969);
 (b) S. N. Hajiev and M. J. Agaranov, *ibid.*, 22, 305 (1970); (c) D. Quane, J. Phys. Chem., 75, 2480 (1971), and references therein.
- [28] (a) R. Walsh and J. M. Wells, Chem. Comm., 513 (1973); (b) S. J. Bond, I. M. T. Davidson, and C. A. Lambert, J. Chem. Soc. A, 2068 (1968); (c) M. A. Ring, J. Am. Chem. Soc., 90, 4870 (1970); (d) G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, 87, 5329 (1965); (e) W. C. Steele, L. D. Nichols, and F. G. A. Stone, *ibid.*, 84, 4441 (1962); (f) R. Walsh and

J. M. Wells, J. Chem. Soc. Faraday Trans. I, 72, 100, 1212 (1976), and references therein.

- [29] A. Hoska and F. S. Rowland, J. Phys. Chem., 77, 705 (1973).
- [30] (a) J. W. Simons and G. W. Taylor, J. Phys. Chem., 73, 1274 (1969); (b) G. W. Taylor and J. W. Simons, *ibid.*, 74, 464 (1970); (c) G. W. Taylor and J. W. Simons, Int. J. Chem. Kinet., 3, 25 (1971).
- [31] (a) J. R. Durig and C. W. Hawley, J. Phys. Chem., **75**, 3993 (1971); (b) A. Veillard, Chem. Phys. Lett., **3**, 128 (1969); (c) K. C. Ingham, J. Phys. Chem., **76**, 551 (1972); (d) A. B. Harvey, *ibid.*, **70**, 3370 (1966); (e) J. P. Lowe and R. G. Parr, J. Chem. Phys., **44**, 3001 (1966); (f) M. S. Gordon and L. Neubauer, J. Am. Chem. Soc., **96**, 5690 (1974).
- [32] D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. C. Powell, J. Chem. Phys., 25, 736 (1956).

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