photolysis measurements). These values correspond to values obtained for the analogous Ru(IV) complex $[(\text{tpy})(\text{bpy})\text{Ru}^{\text{IV}}{=}\text{O}]^{2+}$[28] for which $\epsilon_{471} = 550\ \text{M}^{-1}\ \text{cm}^{-1}$ and $\epsilon_{436} = 1150\ \text{M}^{-1}\ \text{cm}^{-1}$.

It seems, therefore, that the values of the rate constants are consistent with comparable electron-exchange and proton-transfer processes, and that the extinction coefficients of the proposed intermediate are consistent with those of a comparable Ru(IV) species. It should be stressed that the curve-fitting procedure produced two numerical solutions, one of which appears to be marginally more satisfactory. The consistency in the values of all variables, and particularly of k_6 on variation of both acid and Ru(III) concentration, leads us to have considerable confidence in the method. The method is quite sensitive to changes in the quoted values of the rate constants: in particular, for the fit to be maintained between the calculated and observed responses, the values of k_1, k_6, ϵ, and the ratio k_2/k_3 are critical and are required to be within 10% of the values quoted. The rate constants k_4 and k_5 are less critical (±25%). Although the ratio k_2/k_3 must be within 10%, the actual values of the individual rate constants, k_2 and k_3, may vary by a factor of 2.

Conclusions

The particular efficacy of Ru in the promotion of the oxidative dehydrogenation of an amine such as 2-(aminomethyl)pyridine seems related to its ability to readily attain an oxidation state 2 units greater than the final state, allowing a low-energy pathway for the even-electron process required in these dehydrogenation reactions. We are presently extending these methods of flash photolysis and electrochemistry to other oxidative dehydrogenation reactions to examine the generality of the scheme for ruthenium complexes containing other amines and alcohols and to assign unambigously the mechanistic schemes for such reactions involving alternative metal centers.

Acknowledgment. We wish to acknowledge the Australian Institute of Nuclear Science and Engineering for the use of stopped-flow facilities of the Australian Atomic Energy Commission, Lucas Heights. We are grateful to the Department of Physical and Inorganic Chemistry, University of Adelaide, for the use of the flash photolysis facilities, and particularly to Dr. G. S. Laurence and Ms. P. Ashwood for their assistance. We thank the Australian Research Grants Committee for supporting this research.

Appendix

Analysis of Experimental Data. In view of the complexity of the reaction mechanisms proposed in the study, analytical solution of the rate law equations was not possible: a numerical technique was required in order to analyze the experimental responses.

The numerical problem is to solve systems (up to 7) of coupled differential equations which define the rate laws. Due to the large possible variation in the magnitude of the rate constants within the proposed mechanism, the coupled differential equations are "stiff",[40] and conventional numerical differential equation algorithms such as the Runge–Kutta algorithm cannot efficiently be used. Algorithms have been specifically designed for the solution of stiff sets of equations of which the method of Gear, used in this study, is in most common use (IMSL library routine DGEAR[41]).

Kinetic information is available from the experimental responses by finding the set of rate constants for a given mechanism which minimize the sum of squares difference between the predicted and experimental response. Nonlinear programming (NLP) techniques automatically vary the rate constants such that this minimum is obtained rapidly. The two NLP techniques used were the simplex algorithm and a Marquadt Steepest Descent algorithm, the latter being the more efficient, but both were found to converge to the same solutions for certain problems, thus confirming the validity of the results.

The possibility of local rather than global optima having been reached was diminished by supplying largely varying initial values of the rate constants and observing convergence to the same optimal solution.

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The Mechanism and Kinetics of the Homogeneous Gas-Phase Thermal Decomposition of Methylgermane

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Abstract: The homogeneous gas-phase decomposition of methylgermane has been investigated by the comparative rate–single-pulse shock tube technique at 3100 torr of total pressure between 1050 and 1250 K. Three primary processes occur: $\text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_3\text{GeH} + \text{H}_2$ (1), $\text{CH}_3\text{GeH}_3 \rightarrow \text{CH}_4 + \text{GeH}_2$ (2), and $\text{CH}_3\text{GeD}_3 \rightarrow \text{CH}_2{=}\text{GeD}_2 + \text{HD}$ (3). The overall decomposition rate constant in its pressure falloff regime is $\log k_0\ (\text{s}^{-1}) = 13.34 - 50\,420 \pm 3700\ \text{cal}/\theta$, comprised of about 40% of reaction 1, and 30% each of reactions 2 and 3; and the high-pressure rate constants for the primary processes, obtained by RRKM calculations, are $\log k_1\ (\text{s}^{-1}) = 14.6 - 50\,400\ \text{cal}/\theta$, $\log k_2\ (\text{s}^{-1}) = 14.9 - 51\,600\ \text{cal}/\theta$, and $\log k_3\ (\text{s}^{-1}) = 14.7 - 51\,600\ \text{cal}/\theta$. The decomposition of the primary product methylgermylene (CH_3GeH) to $\text{CH}_3\cdot$ and GeH radicals increases with increasing temperature with an activation energy of about 53 kcal, while the decomposition of germylene (GeH_2) to Ge and H_2 is fast and complete at shock temperatures.

Comparisons of the decompositions of silicon and germanium compounds reveal some interesting similarities and also some interesting differences. For instance, both silane (SiH_4) and germane (GeH_4) decompose by a three-center hydrogen elimination process to produce singlet diradicals (silylene, SiH_2:, and germylene, GeH_2:).[1,2] However, under static system pyrolysis conditions ($T \sim 600$ K), the silane decomposition is homogeneous[3] (at least in the initial stages), while the germane decomposition appears to be mainly heterogeneous.[2] Both group 4 hydride decompositions have stoichiometries approaching $(\Delta(\text{H}_2)/\Delta$-

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$(MH_4)) \simeq 2$,[1,2] indicating eventual production of hydrogen from the diradical primary products. The modes of this production, however, differ. Germylene is unstable and can eliminate hydrogen directly in a subsequent decomposition step.[2] Silylene, by contrast, is rather stable and produces hydrogen as a result of polymerization, either at the walls or in a homogeneous manner.[1]

In a continuing effort to investigate the contrasting kinetic behaviors of silicon and germanium compounds, we report here an investigation of the stoichiometry, products, mechanism, and kinetics of the shock-induced thermolysis of methylgermane. Points of comparison are provided by two prior kinetic investigations of the thermal decomposition of methylsilane. Neudorfl and Strausz[4] have investigated the CH_3SiH_3 pyrolysis by static methods in the 40–400 torr pressure and 613–713 K temperature ranges. In the presence of ethylene, first-order reaction rates were significanttly reduced (indicating some free radical component to the uninhibited decomposition system), and the kinetics were well fitted by the Arrhenius relation

$$\log k_{CH_3SiH_3}\ (s^{-1}) = 14.95 \pm 0.11 - (63\,200 \pm 330\ \text{cal})/2.3RT$$

The primary process was thought to be the H_2 elimination reaction (1′). In a low-pressure pyrolysis of methylsilane, at pressures

$$CH_3SiH_3 \rightarrow CH_3\ddot{Si}H + H_2 \qquad (1')$$

below 0.1 torr between 898 and 1000 K, Davidson and Ring[5] obtained, for the kinetics of reaction 1′, $\log k_{1(CH_3SiH_3)} = 14.1 - 64\,800/2.3RT$. Under these conditions the reaction is almost certainly in the pressure falloff regime. Equally important was the observation of a second primary decomposition process, reaction 2′. While this methane molecular elimination process could

$$CH_3SiH_3 \rightarrow CH_4 + SiH_2\colon \qquad (2')$$

not be accurately evaluated, from the methane to hydrogen product yield variations, Ring and Davidson were able to establish the approximate Arrhenius parameters, $\log A_2$ (s^{-1}) = 13.6 and $E_2 \simeq 68$ kcal. The subsequent roles in the decomposition mechanism of the silylene products ($SiH_2\colon$ and $CH_3\ddot{Si}H$) were not established.

With the exception of pyrolysis product information from a flow system investigation,[6] very little is known about the methylgermane thermolysis. The products observed (H_2, CH_4, $(CH_3)_2GeH_2$, and small quantities of $(CH_3)_2Ge_2H_4$) are generally similar to products observed in the decomposition of methylsilane, and hence a similar reaction mechanism seems likely. However, since the germane decomposition is heterogeneous under the same experimental conditions, it would be dangerous to place too much confidence in this reaction analogy. Therefore, we have investigated the decomposition of CH_3GeH_3 by the single-pulse shock tube–comparative rate technique with three principle objectives: (1) to establish the primary processes of the homogeneous gas-phase decomposition; (2) to evaluate the Arrhenius parameters of the various primary processes; and (3) to determine the subsequent reaction pathways of the reactive primary products (presumably germylenes).

Experimental Section

The single-pulse shock tube used in this study is similar to that described by Jeffers and Shaub,[7] and it has been previously described by us.[1] Arrival times of the shock and rarifaction waves were monitored by a Kistler Model 211 B-3 pressure transducer, along with a Kistler 549 piezotron coupler, a Tektronix 545A oscilloscope, and a C-12 camera system. Shock waves were monitored by the rupture of 0.5 mil mylar diaphrams with a magnetically driven pin. Product sampling was made immediately after the shock and was confined to a 18 cm^3 gas volume extracted at a port at the end plate.

Table I. Total Hydrogen and Hydrogen Deuteride Yield Data

temp,[c] K	% decomp[d]	Δ(total hydrogen)/ $\Delta(CH_3GeH_3)$[a,e]	Δ(HD)/ $\Delta(CH_3GeD_3)$[b,e]
1069.4	27.2	1.147	0.218
1086.2	36.8	1.176	0.223
1088.6	38.3	1.173	0.223
1091.5	40.2	1.249	0.237
1121.0	61.2	1.247	0.237
1145.2	78.3	1.227	0.233
1163.0	88.3	1.377	0.262
1174.6	93.0	1.389	0.264

[a] Hydrogen yield data from the reaction of CH_3GeH_3 in toluene (H_8). [b] Δ(HD)/Δ(MG) was obtained from measurements of HD/total H_2 from data of reactions of CH_3GeD_3 in toluene (H_8) and the results of column 3. [c] ±0.1 K. [d] ±2.5%. [e] ±3.0%.

The various reaction mixtures examined (see later) all had comparable compositions: 0.29 ± 0.01% CH_3GeH_3, 0.28 ± 0.02% xenon (the mass spectrometric standard), 0.14 ± 0.01% C_2H_4 (the GLC standard), 0.13% cyclopropane (used as the comparative standard), and from 2.5–3.7% toluene (used as a free radical trapping agent). The diluent was Argon. Four different isotopically labeled mixtures were examined: no. 1, CH_3GeH_3 + $PhCH_3$; no. 2, CH_3GeH_3 + toluene (D_8); no. 3, CH_3GeD_3 + $PhCH_3$; no. 4, CH_3GeD_3 + toluene (D_8). Reaction temperatures ranged from 1047 to 1225 K, and shock times measured at the end plate, varied from 220 to 335 μs. Pressures of note were driver section (40 psig), test section (70–142 torr), and reaction pressures (3070 ± 100 torr).

Reactants (CH_3GeH_3 and cyclopropane) and products (CH_4, C_2H_6, propylene, benzene, and ethylbenzene) were analyzed by GLC relative to the internal standard, C_2H_4, using a $^1/_8$ in. × 10 ft Poropak Q column and a Varian 1400 FID chromatograph coupled to a Hewlett-Packard 3380 A electronic digital integrator. Manual temperature programming was required for the higher molecular weight compounds. The benzene and ethylbenzene analyses were confirmed on a $^1/_8$ in. × 6 ft 8% Carbowax on Chromasorb w column operated at 30 °C. Decomposition of methylgermane in the absence of ethylene did not produce ethylene. Also, mixtures of C_2H_4 and toluene shocked under the methylgermane reaction conditions did not produce any organic products.

The products H_2, HD, D_2, and CH_3D were analyzed mass spectrometrically [See J. Dzarnoski's Ph.D. thesis for more details.] relative to the internal standard xenon. The *m/e* peaks used were 2, 3, 4, 17, and 131, respectively. While GeH_4 is readily detectable by MS methods, no GeH_4 was detected in the products of the CH_3GeH_3 decompositions.

Component sensitivity factors for the GLC and MS analyses were obtained from standard mixtures of authentic samples.

Rate constants for the methylgermane and cyclopropane (Δ) decompositions were obtained from the relations

$$k_{CH_3GeH_3} = \frac{1}{\tau} \ln \frac{(CH_3GeH_3/C_2H_4)_0}{(CH_3GeH_3/C_2H_4)_t}$$

$$k_\Delta = \frac{1}{\tau} \ln \frac{1}{[1 - CH_2CHCH_3/CH_2CHCH_3 + \Delta]}$$

where τ is the shock time recorded by the pressure transducer and the sub 0 and *t* notations indicate concentrations appropriate to the initial reaction mixtures and the final shocked mixtures, respectively.

Methylgermane was prepared from reaction of CH_3I with $KGeH_3$,[8] while CH_3GeD_3 was prepared by reduction of CH_3GeCl_3 with $LiAlD_4$. The reagents were purified by trap to trap distillation and their purity established by infrared, mass spectral, and GLC analyses.

Results

Products of the methylgermane decomposition in the presence of excess toluene were H_2, CH_4, C_2H_6, and trace quantities of benzene. No germane was detected, and only trace quantities of ethylbenzene at near complete decomposition were observed. Data relevant to the reaction stoichiometry are shown in Tables I–III. Table I shows how hydrogen produced relative to CH_3GeH_3 decomposed varies with percent decomposition. An increase is apparent: $\Delta(H_2)/\Delta(MG) = 1.15$ (27% reaction); $\Delta(H_2)/\Delta(MG)$

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Chart I

	Addenda		
⬢	TOTAL HYDROGEN/Δ(MG)	CH_3GeH_3	TOLUENE H-8
○●	D_2/(MG)	CH_3GeD_3	TOLUENE D-8
□	(HD + 0.30)/Δ(MG)	CH_3GeD_3	TOLUENE D-8
△	CH_4/Δ(MG)	CH_3GeH_3	TOLUENE D-8
■	HD/Δ(MG)*	CH_3GeD_3	TOLUENE H-8
◆	$\Sigma CH_3\bullet/\Delta(MG)$[≠]	CH_3GeH_3	TOLUENE D-8

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*Based on independent measurements of:

$$\frac{\text{TOTAL HYDROGEN FORMED}}{\text{MeGeH}_3\text{ LOST}} \text{ and } \text{HD}/[\text{HD} + \text{D}_2]$$

[≠] $[CH_3D + 2[C_2H_6]]/\Delta(MG) = \Sigma CH_3\bullet/\Delta(MG)$

Table II. D_2 and HD Product Yields[a]

temp,[b] K	% decomp[c]	$\Delta(D_2)/\Delta(MG)$[d]	Δ(HD)/Δ(MG)[d]	Δ(total hydrogen)/Δ(MG)[d]
1053.8	24.0	0.902	0.361	1.263
1064.9	30.0	0.743	0.270	1.013
1095.1	48.8	0.739	0.292	1.031
1101.1	53.2	0.864	0.360	1.224
1102.5	54.2	0.782	0.293	1.075
1107.3	57.3	0.867	0.265	1.132
1128.0	72.7	0.867	0.350	1.217
1134.0	76.8	0.843	0.344	1.187
1142.8	82.4	0.766	0.294	1.060
1140.2	81.2	0.927	0.304	1.231
1151.1	87.0	0.873	0.352	1.225
1174.8	96.4	0.946	0.319	1.265
1172.5	95.6	1.102	0.343	1.444

[a] Yield data from reactions of CH_3GeD_3 in toluene (D_8). [b] ±0.1 K. [c] ±2.5%. [d] ±3.0%.

= 1.38 (93% reaction). Also shown are HD yield data from shocks of CH_3GeD_3 in toluene (H_8). For more data concerning the possible participation of hydrogen atoms to be obtained, studies of the (HD/D_2) produced on shocking mixtures of CH_3GeD_3 in toluene (D_8) were made. These data are also shown in Table II. Data relevant to methane production are shown in Table III. These data were obtained from shocks of CH_3GeH_3 in the presence of excess toluene (D_8). If we reasonably assume that methyl radicals abstract hydrogen exclusively from toluene, then the CH_4 yields are measures of methane produced in some molecular elimination from methylgermane. This could occur via either a primary or a secondary decomposition mode. Similarly, CH_3D and ethane are clear measures of methyl radical production.

The data are perhaps best examined relative to Chart I, which shows product yields of total hydrogen, molecular methane, methyl radical, HD, and D_2 relative to methylgermane losses with percent decomposition. In the following, we analyze the product data in terms of a number of reaction possibilities. These are shown in Scheme I.

Scheme I

Possible Primary Processes

$$CH_3GeH_3 \rightarrow CH_3GeH + H_2 \tag{1}$$

$$CH_3GeH_3 \rightarrow CH_4 + GeH_2 \tag{2}$$

$$CH_3GeH_3 \rightarrow H_2 + CH_2{=}GeH_2 \tag{3}$$

$$CH_3GeH_3 \rightarrow CH_3\cdot + GeH_3\cdot \tag{4}$$

Possible Secondary Processes

$$GeH_2 \rightarrow Ge + H_2 \tag{5}$$

$$GeH_2 \rightarrow \cdot GeH + H\cdot \tag{6}$$

$$CH_3GeH \rightarrow CH_3\cdot + \cdot GeH \tag{7}$$

$$CH_3GeH + (CH_3GeH, R\cdot) \rightarrow \text{polymer} \tag{8}$$

$$CH_3GeH \rightarrow CH_4 + Ge \tag{9}$$

$$GeH + \text{polymer} \rightarrow GeH_2 + \text{polymer-H} \tag{10}$$

Possible Free Radical Trapping Reactions

$$H\cdot + PhCH_3 \rightarrow \cdot CH_3 + PhH \tag{11}$$

$$H\cdot + PhCH_3 \rightarrow H_2 + PhCH_2\cdot \tag{12}$$

$$H\cdot + CH_3GeH_3 \rightarrow H_2 + CH_3GeH_2\cdot \tag{13}$$

$$H\cdot + C_2H_4 \rightleftarrows \cdot C_2H_5 \tag{14}$$

$$\cdot CH_3 + PhCH_3 \rightarrow CH_4 + PhCH_2\cdot \tag{15}$$

$$\cdot CH_3 + CH_3GeH_3 \rightarrow CH_4 + CH_3GeH_2\cdot \tag{16}$$

$$\cdot CH_3 + C_2H_4 \rightleftarrows \cdot CH_3CH_2CH_2\cdot \tag{17}$$

Methyl Radical and Molecular Methane Formation. The question most crucial to the understanding of the methylgermane decomposition mechanism concerns the methyl radical source. Are methyl radicals produced mainly in a primary process (reaction 4), or are they produced in some secondary reaction like reaction 7?

If one assumes that methyl radicals are produced solely by reaction 4, a typical Arrhenius plot of $\ln[\Delta(CH_3)/\Delta(MeG)]$ vs. $1/T$ will give a slope related to the experimental activation energy of this methyl radical formation reaction relative to the overall methylgermane decomposition activation energy [yield of $CH_3/\Delta(MeG) = \int_0^\tau k_4[MeG]dt/\int_0^\tau k_{MeG}[MeG]dt = k_4/k_{MeG}$] (see Figure 2). The result is $(E_4 - E_{MeG}) = -\text{slope} \times R = 51.0$ kcal/mol. Since $E_{MeG} = 50.4$ kcal (see later), one obtains $E_4 = 101.4$ kcal, which is a value significantly higher than the thermochemically estimated high-pressure limiting value of about 80

Table III. Hydrocarbon Yield Data[a]

temp,[b] K	% decomp[c]	$\Delta(CH_4)/\Delta(CH_3GeH_3)$[c]	$\Delta(CH_3D)/\Delta(CH_3GeH_3)$[d]	$\Delta(C_2H_6)/\Delta(CH_3GeH_3)$[c]	$\Delta(CH_3\cdot)/\Delta(CH_3GeH_3)$[d]	$\ln[10\Delta(CH_3\cdot)/\Delta(MG)]$
1083.7	28.1	0.289	0.048	0.023	0.094	−0.062
1111.8	44.9	0.309	0.060	0.055	0.170	0.531
1118.3	48.5	0.282	0.069	0.055	0.179	0.582
1118.2	49.3	0.298	0.070	0.054	0.178	0.577
1123.0	52.7	0.284	0.061	0.052	0.165	0.501
1131.0	58.5	0.294	0.082	0.059	0.200	0.693
1143.5	67.4	0.285	0.095	0.082	0.259	0.952
1141.9	68.0	0.297	0.093	0.079	0.251	0.920
1149.8	80.1	0.277	0.138	0.103	0.344	1.235
1150.4	79.3	0.294	0.137	0.100	0.337	1.215
1030.3	9.3		0.021		0.021	−1.561

[a] Obtained from product analyses of reactions of CH_3GeH_3 in toluene (D_8). [b] ±0.1 K. [c] ±2.5%. [d] ±3.0%.

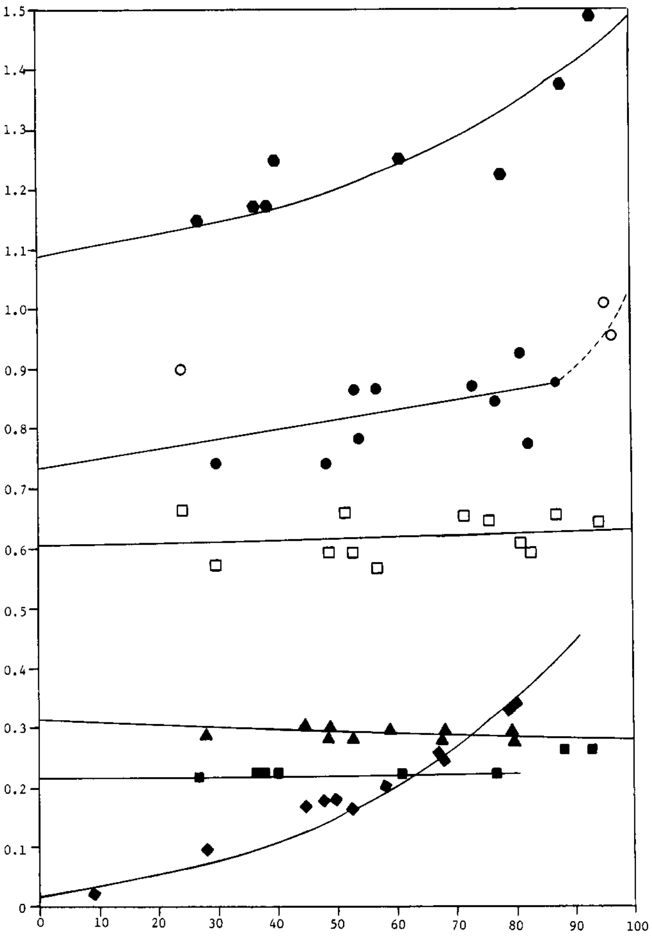


Figure 1. Product yields vs. percent decomposition.

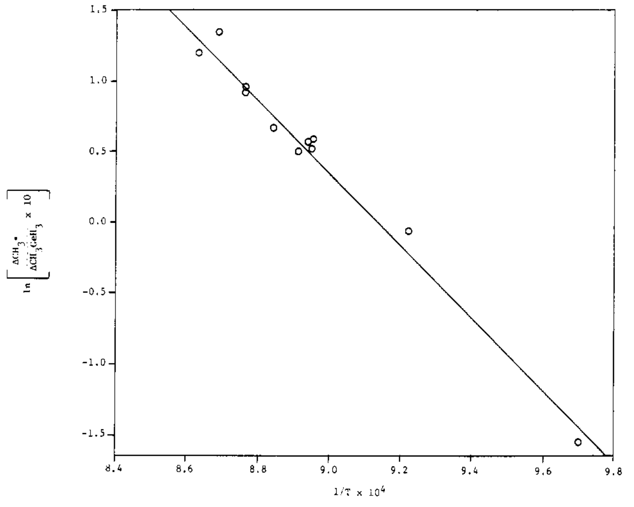


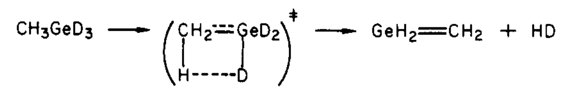
Figure 2. Relative Arrhenius plot to test the possibility of (C–Ge) bond fission as a primary process of the methylgermane decomposition.

kcal.[9] Further, the observed rates of methyl radical production are from 10^2 to 10^3 times faster than those expected on the basis of estimates of the high-pressure Arrhenius parameters from reaction 4 (i.e., $A_4 \simeq 10^{16.5}$ s^{-1}, $E_4 \simeq 80$ kcal) and at least another order of magnitude faster than the estimated pressure falloff rates of reaction 4 under our reaction conditions. We therefore conclude that reaction 7 is the source of methyl radicals, not reaction 4. Supporting this conclusion is the fact that all efforts to detect germane in the reaction products failed. [Germyl radicals produced via reaction 4 would be expected to abstract H from toluene in our systems to form germane.] If methyl radicals are produced via reaction 7, then molecular methane must be formed via reaction 2. The two products cannot have a common source because of the large activation energy difference implied by the data for their formation reactions if competitive. [$\Delta(CH_3)/\Delta(CH_4)_{molec} = (\Delta(CH_3\cdot)/\Delta(MeG))(\Delta(MeG)/\Delta(CH_4)_{molec})$. Since $\Delta(MeG)/\Delta(CH_4)_{molec} \simeq 1/0.3$ (T independent) and ln $(\Delta(CH_3\cdot)/\Delta(MeG))$ vs. $1/T$ shows an activation energy difference of 51.0 kcal, if competitive, E($CH_3\cdot$ formation) − E(molecular methane formation) $\simeq$ 51 kcal.] Reliable Arrhenius parameters for reactions 11–13 are not available. However, E_{11} appears to be 4 kcal/mol[10] while E_{13} is probably less than E_{11}.[11] Thus under our reaction conditions, reactions 13 and 14[12] could be competitive (but not significantly faster) with reaction 11. However, benzene production (reaction 11) was minimal even at very high percent decompositions. Thus reactions 13 and 14 were also of minor importance. In addition, the lifetime of $\cdot C_2H_5$ (from reaction 14) is about 10 μs at 1100 K.[12]

With an estimate of E_{16} based on the CH_3 radical abstraction reaction with CH_3SiH_3[13] and a value of E_{15} for $C_6H_5CD_3$,[14] it would appear that reaction 16 could be competitive with reaction 15 under our reaction conditions. However, if one examines the results in Table III, it is clear that below 50% $MeGeH_3$ decomposition, reaction 15 (CH_3D yield) is a minor reaction and that reaction 16 occurs to a less extent than reaction 15. If significant CH_4 were produced via reaction 15, the ratio $\Delta(CH_4)/\epsilon(CH_3GeH_3)$ would increase significantly with percent decomposition. The data in Table III demonstrate the yield was indeed constant within experimental error. In addition the lifetime of $CH_3CH_2CH_2\cdot$ (product of reaction 17) is less than 0.1 μs at 1000 K and therefore reaction 17 is not important.

Thus it appears that in the methylgermane decomposition, just as in the methylsilane system, both H_2 and CH_4 are produced directly in concerted, three-center, molecular elimination reactions.

Hydrogen Deuteride Production. For a test of the possible participation of hydrogen atoms in the eventual formation of the hydrogen product, a series of shocks on reaction mixture 3 (CH_3GeD_3 + toluene) were made. Large yields of HD were found (see Table I), but the relative insensitivity of the HD/Δ(MeG) ratios to temperature changes were difficult to rationalize in terms of D atoms. In addition we noted that below 38% decomposition, the difference in ratios (Δ(total hydrogen)/Δ(MeG) − Δ(HD)/Δ(MeG)) was less than 1.0 (see Table I). This difference would have to be at least unity *if* reactions 1 and 2 were the *only* primary processes. [GeD_2 produced in reaction 2 quantitatively eliminated D_2 via reaction 5.[2]] We therefore concluded that HD might be produced via a four-center molecular elimination, reaction 18. A series of shocks on reaction mixture 4 (CH_3GeD_3 + toluene-d_8) were then made. D atoms in this system must yield only D_2, and HD can only arise via the above elimination reaction. Similar large yields of HD, and D_2 yields below 1.0, were found (Table II), and hence the above unexpected and unusual four-center molecular elimination reaction does occur in the methylgermane decomposition.



$$CH_3GeD_3 \longrightarrow \left(\begin{matrix} CH_2 \cdots GeD_2 \\ | \quad\quad | \\ H \cdots\cdots D \end{matrix}\right)^{\ddagger} \longrightarrow GeH_2{=}CH_2 + HD \quad (18)$$

Primary Processes in the Methylgermane Decomposition. There are therefore three primary processes in the methylgermane decomposition: a three-center H_2 elimination (reaction 1), accounting for about 40% of the overall reaction; a three-center

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(9) Based on preliminary data from our studies on the decomposition of $(CH_4)_4Ge$.

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molecular elimination of CH_4 (reaction 2), accounting for about 30% of the overall reaction; and a four-center hydrogen elimination (reaction 3), accounting for about 30% of the reaction. The degree of importance of the latter two processes is surprising, particularly the four-center H_2 elimination process for which, to our knowledge, there is few proven procedents in hydrocarbon systems. Four-center elimination reactions are thought to proceed via polar transition states[16] with alternating charge polarities (as shown in reaction 18). The hydridic character of the germyl hydrogens is consistent with this type of polarization. That four-center hydrogen eliminations have not been much observed in hydrocarbon systems is probably due to the difficulty of detecting the reaction in the presence of other faster and dominant reaction processes (i.e., free radical induced decomposition reactions of long-chain length). However, Benson and Haugen,[17] via a self-consistent electrostatic model for the prediction of the activation energies of four-center addition reactions, have estimated activation energies of 41.3, 36.7, and 29.3 kcal/mol for H_2 additions to C_2H_4, C_3H_6, and i-C_4H_8, respectively. This implies, as they have noted, that hydrogen elimination may be an important primary process in hydrocarbon decompositions, particularly in highly branched systems. For ethane, one can estimate from the thermochemistry that $k(C_2H_6 \rightarrow C_2H_4 + H_2) \simeq 10^{13.0}e^{-73.6/RT}\ s^{-1}$. At 1000 K, the relative rates of bond fission to dehydrogenation are therefore calculated to be

$$\frac{k(\text{fission})}{k(H_2\ \text{elim})} \simeq \frac{10^{16.75}e^{-89.5/RT^{18}}}{10^{13.0}e^{-73.6/RT}} \simeq \frac{1.9}{1}$$

or about 34% H_2 elimination. This compares very closely to the amount of H_2 elimination observed in methylgermane.

Mass Balances. Mass balances relative to carbon are reflected in the $(\Delta(\sum(CH_3\cdot)) + \Delta(CH_4)_{\text{molec}})/\Delta(\text{MeG})$ ratios. Figure 1 shows that these ratios are about ~0.30 at the lowest temperatures (i.e., low % decompositions) and rise to 0.65 ± 0.05 at the highest temperatures. This suggests that the methylgermylenes produced directly in reaction 1 and indirectly in reaction 3 (i.e., $CH_2{=}GeH_2$ probably isomerizes rapidly to $CH_3\ddot{G}eH$) mainly polymerize at the lower temperatures but begin to decompose to methyl and $\cdot$GeH radicals as the temperatures rise. Since the Ge—H bond strength of the $\cdot$GeH radical is supposed to be greater than 76 kcal/mol,[19] GeH is not expected to decompose. Our data suggest, see below, that GeH radicals abstract hydrogen from the $(CH_3GeH)_x$ polymer (reaction 10) and then decompose to Ge + H_2.

Mass balances on hydrogen products relative to the three primary processes are good considering the difficulties encountered in quantitative MS measurements on isotopically labeled hydrogen. Thus the relative D_2 yields from the shocks of mixture number 4 should be given by

$$\Delta(D_2)/\Delta(\text{MeG}) \leq k_1/k_0 + k_2/k_0 + \sum(CH_3\cdot)/\Delta(\text{MeG})$$

where the inequality and third term on the RHS arise from the subsequent production of D_2 from GeD radical reactions. The data are in good agreement with this relation. Thus at $T \simeq 1080$ K, $\Delta(D)_2/\Delta(\text{MeG}) \leq 0.40 + 0.29 + 0.33 \leq 1.02$ (observed values are about 1.0). It would appear from the above that almost all of the GeD radicals produced eventually generated D_2 in our system.

Activation Energy of Methyl Radical Elimination from CH_3GeH. If we pursue the assumption that the CH_3GeH radicals produced in the primary processes which do not decompose via reaction 7 eventually dimerize or polymerize via reactions like (8), then it is possible to get a rough estimate of the activation energy of the decomposition reaction (7). Thus assuming dimerization as the major CH_3GeH reaction pathway at 1084 K (where $\Delta(CH_3\cdot)/\Delta(\text{MeG}) \simeq 0.09$), one can estimate a methylgermylene steady-state concentration of about $[CH_3GeH]_{ss} \simeq [(k_1 + k_3)(\overline{\text{MeG}})/k_8]^{1/2} \simeq 1.9 \times 10^{-6}$ M, using $(k_1 + k_3) \simeq 1.04 \times 10^4\ s^{-1}$ (see later), $k_8 = 3 \times 10^{10}\ M^{-1}\ s^{-1}$, and $[\overline{\text{MeG}}] \simeq 1.0 \times 10^{-4}$ M. At 1083 K, the relative rate of dimer to methyl radical production from the stoichiometry is

$$\frac{y(\text{dimer})/t}{y(CH_3\cdot)/t} \simeq \frac{[(k_1 + k_3)/k_0 - 0.09]/2}{(0.09)} = \frac{k_8[CH_3GeH]}{k_7} \simeq 3.4$$

Assuming $A_{7(\infty)} \simeq 10^{16.0}\ s^{-1}$, $k(\text{exptl})/k_\infty$ (1083 K, 3100 torr) $\simeq 0.1$, and $k_8 \simeq 3 \times 10^{10}\ M^{-1}\ s^{-1}$, one estimates $E_{7(\infty)} = 53.4 \pm 5$ kcal. This is certainly a reasonable value, although subject to considerable error. The methyl radical production data suggest a somewhat larger activation energy, but we believe that this is caused by methyl radical formation from some other species (perhaps the $(CH_3GeH)_x$ polymer) at the higher temperatures. The D_2 yields also show an accelerated formation rate at the higher temperatures (see dotted line of Figure 1).

Arrhenius Parameters of the Comparative Rate Standard Cyclopropane. Cyclopropane is a small molecule, and hence its isomerization reaction can be subject to pressure falloff effects. At ordinary static system temperatures, falloff has been observed at pressures around 200 torr.[20] The degree of falloff, expressed as k_{uni}/k_∞, is most sensitive to temperature and the energy exchange collision efficiencies (β_c) of the bath molecules; i.e., k_{uni}/k_∞ decreases with increasing T and decreasing β_c. There is evidence that collision efficiencies may be strongly temperature dependent,[21-23] and it has been suggested[23] that the striking curvature in Arrhenius plots for the cyclopropane reaction at temperatures above 1250 K utilizing data from noncomparative rate shock tube studies[24,25] could be due in part to drastically decreasing collision efficiencies. Jeffers, Lewis, and Sarr[26] have investigated this effect in comparative rate studies of cyclopropane against *tert*-butyl alcohol and *cis*-2-butene. They found that the ln k_Δ vs. ln k_s plots were well behaved up to temperatures of 1300 K, and it now appears that the anomolous Arrhenius rate constant–temperature behaviors of cyclopropane are best explained in terms of boundary layer, wall-cooling effects.[27,28] Thus cyclopropane can be employed as a rate standard in shock tube comparative rate studies. However, since cyclopropane is in its pressure falloff regime under shock conditions, the effective Arrhenius parameters will be lower than the high-pressure values, and the effective parameters will be mainly dependent on the β_c values of the bath molecules. Lewis et al.[29] have addressed this problem via extensive comparative rate studies of cyclopropane (Δ) vs. cyclohexene. They studied seven different shock mixtures under varying total pressure and composition conditions and found that best fits of the data were achieved for $\beta_c(\text{Ar}) = 0.05 \pm 0.03$ relative to $\beta_c(\Delta) = 1.0$. On this basis and with the assumption of high-pressure parameters for cyclopropane at 700 K of $\log k_{\Delta(\infty)} = 15.20 - 65000/4.576T$,[18]

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Table IV. Kinetic Data for the Decomposition of Methylgermane and Cyclopropane

temp,[b] K	ln $k(\mathrm{MeGeH_3})$[a]	ln $k(\mathrm{c\text{-}C_3H_6})$[a]
1065.3	6.751	4.120
1080.8	7.132	4.546
1114.8	7.869	5.441
1160.4	9.013	6.560
1189.4	9.333	7.226
1225.4	9.879	8.010
1186.6	9.261	7.163
1148.1	8.817	6.268
1061.0	7.096	4.000
1070.6	7.127	4.267
1084.8	7.444	4.654
1094.8	7.535	4.923
1097.5	7.376	4.993
1127.4	8.123	5.759
1120.6	8.116	5.859
1138.0	8.380	6.021
1144.4	8.544	6.177
1177.3	9.192	6.952
1142.4	8.604	6.129
1186.8	9.419	7.167
1159.0	8.784	6.527
1212.6	9.958	7.737
1211.2	9.776	7.708
1225.1	10.082	8.003
1205.6	9.497	7.585
1059.5	6.914	3.955
1047.4	6.500	3.610

[a] ±1.3%. [b] ±0.1 K.

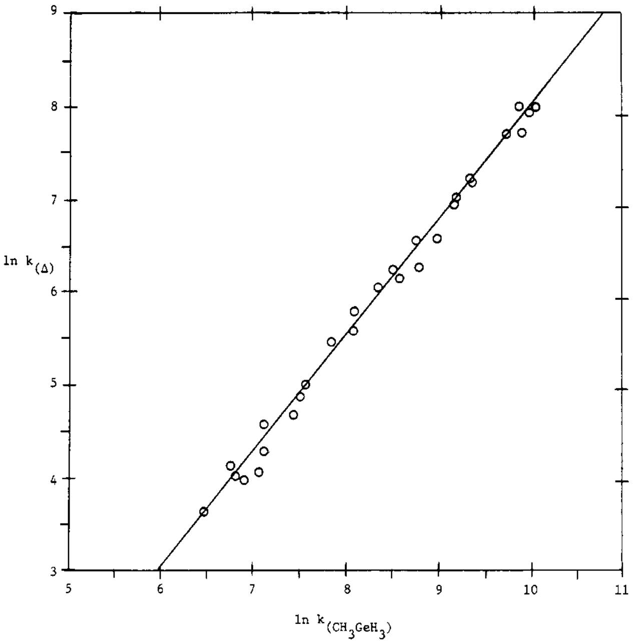

Figure 3. Comparative rate plot of ln k_Δ vs. ln $k_{\mathrm{CH_3GeH_3}}$.

we obtain (through RRKM-falloff calculations) the effective Arrhenius parameters for cyclopropane under our shock reaction conditions of log k_Δ (3100 torr, 1050–1250 K) ($\mathrm{s^{-1}}$) = 14.72 – 63 040 cal/*RT*.

Arrhenius Parameters of the Primary Processes for the Methylgermane Decomposition. Data relevant to the kinetics of the overall decomposition of methylgermane are given in Table IV. The comparative rate plot of ln k_{MeG} vs. ln k_Δ is shown in Figure 3. A least-squares treatment of the data gives a slope of $E_\Delta/E_{\mathrm{MeG}} = 1.2502 \pm 0.059$, where the uncertainty corresponds to the 2.064σ, 95%, confidence limit. This gives for the overall thermal decomposition of methylgermane, $k_{0(\mathrm{MeG})} = (2.21 \times 10^{13})e^{-50\,420\pm3700\ \mathrm{cal}/RT}\ \mathrm{s^{-1}}$.

Table V

A. Calculated (RRKM) Parameters for the Primary Processes of the Methylgermane Decomposition[a,b]

Process 1: Three-Center H_2 Elimination (Reaction 1)
$A_\infty = 3.73 \times 10^{14}\ \mathrm{s^{-1}}$

β_c[d]	β(Ar)	E_1(exptl)	E_∞	E_0
0.3	0.026	51.04	57.55	55.13
0.3	0.020	50.39	57.46	55.05]
0.3	0.015	49.81	57.38	54.96
1.0	0.05	54.46	57.96	55.54

Process 3: Four-Center H_2 Elimination (Reaction 3)
$A_\infty = 8.65 \times 10^{14}\ \mathrm{s^{-1}}$

β_c[d]	β(Ar)	E_3(exptl)	E_∞	E_0
0.3	0.026	52.27	59.81	56.81
0.3	0.020	51.60	59.71	56.71]
0.3	0.015	50.98	59.62	56.61
1.0	0.05	56.02	60.30	57.30

Process 2: Three-Center CH_4 Elimination (Reaction 2)
$A_\infty = 5.05 \times 10^{14}\ \mathrm{s^{-1}}$

β_c[d]	β(Ar)	E_2(exptl)	E_∞	E_0
0.3	0.026	52.26	58.93	56.16
0.3	0.020	51.62	58.85	56.08]
0.3	0.015	51.03	58.76	55.99
1.0	0.05	56.53	60.02	57.25

B. Relative Insensitivity of *E*(exptl) to A_∞[a,c]

Process 2: Three-Center CH_4 Elimination

log A_∞	β_c[d]	β(Ar)	E_2(exptl)	E_∞	E_0
13.0	0.3	0.02	48.76	51.07	51.33
14.7	0.3	0.02	51.62	58.85	56.08
15.2	0.3	0.02	51.80	60.69	56.21

[a] *E*(exptl) are calculated experimental activation energies at 3100 torr of pressure over the temperature range 1050–1250 K. [b] Best fit values indicated by brackets. [c] All energies are in kcal/mol, and *A* factors have units of $\mathrm{s^{-1}}$. [d] All "heavy" molecules: toluene, cyclopropane, and methylgermane. Since "light" gas collision efficiencies appear to be lower (0.05 → 0.02), a similar reduction in the β_c of "heavy" molecules seemed reasonable.

Table VI. Arrhenius Parameters[a,b] of Primary Processes

reaction	*A*(exptl)	*E*(exptl)	$10^{-14}A_\infty$	E_∞
three-center H_2 elimination, (1)	9.1×10^{12}	50.4	3.7	57.6
three-center CH_4 elimination, (2)	1.2×10^{13}	51.6	8.6	59.7
four-center H_2 elimination, (3)	1.1×10^{13}	51.6	5.1	58.9

[a] *A* factors in units of $\mathrm{s^{-1}}$ and *E* in kcal. [b] Experimental parameters are for 3100 torr and 1050–1250 K conditions and are RRKM calculated values based on thermochemical kinetics estimates of the high-pressure *A* factors.

Primary product yields relative to methylgermane loss are direct measures of the ratios of the primary process rate constants to the overall rate constant. Thus, $k_2/k_0 = y(\mathrm{HD})/\Delta(\mathrm{MeG})$, $k_3/k_0 = y(\mathrm{CH_3D})/\Delta(\mathrm{MeG})$, and $k_1/k_0 = (1 - k_2/k_0 + k_3/k_0)$. Arrhenius plots of the functions ln (k_2/k_0) vs. $1/T$ and ln (k_3/k_0) vs. $1/T$ give experimental activation energy differences of $E_2 - E_0 = -1490 \pm 4440$ cal and $E_3 - E_0 = 730 \pm 2700$ cal, and since the errors exceed the slopes, our experimental results are unable to distinguish activation energy differences between the primary processes. In view of the following RRKM calculations, this is not surprising.

The RRKM calculations on the three primary processes of methylgermane were made by employing high-pressure limiting *A* factors estimated by well-known thermochemical kinetic methods.[30] These should be reliable to at least a factor of 3.

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Table VII. Vibration Frequencies[a, b] Used in RRKM Calculations[c]

	transition state for		
reactant	reaction 1	reaction 2	reaction 3
3(2940)	3(2940)	3(2940)	2(2940)
3(2085)	2085	2(2085)	2(2085)
600	600	420	2060
2(850)	2(1460)	1460	1460
2(505)	2(850)	3(1430)	640
3(1430)	505	900	2(925)
3(900)	2(590)	2(600)	2(550)
85	355	2(400)	615
	3(1430)	250	370
	85	235	1450
			900
			595
			235

[a] All frequencies are in units of cm^{-1}. [b] Reactant frequencies given by J. E. Griffiths, *J. Chem. Phys.*, 38, 2879 (1963). Reaction 1 = three-center H_2 elimination, reaction 2 = three-center CH_4 elimination, and reaction 3 = four-center H_2 elimination. [c] RRKM calculational procedure: input k(exptl) at T and P_{total}, collision efficiencies, reactant and transition-state frequencies, and a guessed k/k_∞. An iterrative technique calculates k/k_∞ to 1% accuracy, from which $\Delta E_0{}^{\circ\ddagger}$ and E(exptl) are obtained. Then the k_{uni} vs. P at various temperatures are calculated in the usual manner.[31] State densities and state sums are calculated by using the Beyer-Swinehart alogorithm.[32] Collision diameters of $MeGeH_3{}^{\ddagger}$ with heavy molecules was 5.05 Å while that with Ar was 4.06 Å.

Frequencies used are given in Table VII. The 1083.3 K temperature condition was used as reference, at which temperature $k_0 = 1500$ s^{-1}, composed of $k_1 = 613$ s^{-1}, $k_2 = 453$ s^{-1}, and $k_3 = 434$ s^{-1}. Results of the calculations for the series of collision efficiency pairs are shown in Table VA. Note that the collision efficiencies appropriate to the cyclopropane reaction ($\beta_c(\Delta) = 1.0$, $\beta_c(\text{Ar}) = 0.05$) give activation energies about 4 kcal higher than observed (see Table VA). This is outside our limits of error. This could mean that the bath molecule collision efficiencies for the methylgermane reaction under our shock tube reaction conditions are lower than those for the standard cyclopropane reaction. On this basis, best agreement between calculated and observed activation energies occurs for the conditions $\beta_c(\text{MeG, PhCH}_3) = 0.30$ and $\beta_c(\text{Ar}) = 0.020$. Note also that the calculated differences $E_2 - E_0$ and $E_3 - E_0$ are less than 1.3 kcal (any β_c pair), which is smaller than the experimental errors associated with their measurement.

Calculations for three different transition-state models for the CH_4 elimination process, covering a range of more than 2 orders of magnitude in A_∞ (see Table VB) were made to demonstrate the relative insensitivity of the calculated experimental activation energies to the magnitude of A_∞ and only 0.18 kcal/mol for a variation of a factor of 3 (i.e., the estimated error limit of the A factor estimates).

Arrhenius parameters obtained from the RRKM calculations both for our reaction pressures and for the high pressure limit in the 1050–1250 K range are given in Table V. Activation energies higher by about 2.2 kcal/mol are suggested for the CH_4 and four-center molecular H_2 eliminations as compared to the "usual" three-center molecular elimination process. This seems quite reasonable and is in agreement with the corresponding difference (methane elimination vs. H_2 elimination) reported by Ring and Davidson[5] from their study of the methylsilane decomposition ($E_{CH_4} - E_{H_2} \simeq 4$ kcal/mol).

In summary, we conclude that the primary routes in the homogeneous gas-phase decomposition of CH_3GeH_3 are reactions 1, 2, and 3: $CH_3GeH_3 \rightarrow CH_3GeH + H_2$ (1), $CH_3GeH_3 \rightarrow CH_4 + GeH_2$ (2), and $CH_3GeD_3 \rightarrow CH_2{=}GeD_2 + HD$ (3). The overall decomposition rate constant in its pressure falloff regime is $\log k_0$ (s^{-1}) = 13.34 − 50 420 ± 3700 cal/θ, comprised of about 40% of reaction 1) and 30% each of reactions 2 and 3); and the high-pressure rate constants for the primary processes, obtained by RRKM calculations, are $\log k_1$ (s^{-1}) = 14.6 − 50 400 cal/θ, $\log k_2$ (s^{-1}) = 14.9 − 51 600 cal/θ, and $\log k_3$ (s^{-1}) = 14.7 − 51 600 cal/θ.

Acknowledgment. We are indebted to the Department of Energy for financial support of the work (Grant DE-FG02-80CS83103).

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