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Laser sensitized dissociation of tetramethyl germane

Ann. E. Stanley

Weapons Sciences Directorate, AMSMI-RD-WS-CM Research, Development, and Engineering Center, US Army Missile Command, Redstone Arsenal, AL 35898-5248, USA

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Abstract

Tetramethyl germane was decomposed using laser sensitized photochemistry. Sulfur hexafluoride, a sensitizer, was added to gas phase tetramethyl germane and irradiated using a carbon dioxide, infrared, continuous wave laser under variable experimental conditions. The gas phase reactions were monitored before and after reaction using both Fourier transform infrared spectroscopy and gas chromatographic/mass spectral techniques. End product analysis showed that methane, ethene, and ethyne were the primary gaseous products. Germanium was identified visually as a gray solid. This laser sensitized dissociation of tetramethyl germane was optimized by a variation in irradiations and conditions such as sample pressure including sensitizer to reactant pressure ratio, laser power, and time. The yield of germane at the 1 s irradiation was 33% while at the 5 s irradiation, at 57% was observed. Both the rate of depletion of tetramethyl germane and the rate of formation of methane, ethene, and ethyne were determined at numerous irradiation times. Longer irradiation times and higher sulfur hexafluoride pressures produced higher yields. Experimental data from the time studies were used to generate simulated concentrations of reactants, reactive intermediates, and products as a function of time to a high degree of accuracy. The rate constants for the laser sensitized dissociation of tetramethyl germane using sulfur hexafluoride as a sensitizer were determined. Simulation analysis suggests that this reaction can be fit statistically to an eight-step reaction mechanism. These results are discussed and compared to similar literature studies of tetramethyl germane dissociations

Keywords: Tetramethyl germane; Laser; Sensitizer; Simulation

1. Introduction

The objective of this laser sensitized photochemical investigation of tetramethyl germane is to probe both the kinetics and the process optimization of the laser sensitized dissociation of tetramethyl germane. Previous research [1,2] done in this laboratory with germane and the sensitizer, sulfur hexafluoride, demonstrated that higher yields of germanium can be obtained using laser sensitized photochemistry. Sulfur hexafluoride is a well-known infrared sensitizer which has an extremely high absorptivity that not only results in the absorption of more energy from the laser beam but also can increase the rate of decomposition of the germanium compounds. This analysis will identify qualitatively the compounds which are formed through the laser sensitized dissociation of mixtures of tetramethyl germane and sulfur hexafluoride using a carbon dioxide, infrared, continuous wave laser. Both infrared spectral and gas chromatographic/mass spectral analysis of the laser sensitized dissociation of tetramethyl germane using sulfur hexafluoride will be done to seek the optimal experimental conditions. Simulation analysis of the experimental data will probe the kinetics of this laser sensitized process.

The highest purity germanium is presently obtained by the thermal decomposition of highly pure germane [3,4] under variable conditions [5–10]. The major disadvantage of the thermal technique is the poor yield which rarely exceeds 70%–80% [3]. The production of germanium films using an ultraviolet laser is already known [11]. This technique has the distinct disadvantage that as germanium is deposited, the rate of deposition of germanium decreases due to the opaqueness of the germanium film to the ultraviolet light. However, germanium is itself transparent to infrared light, making the carbon dioxide laser a better candidate for laser formation since the sensitizer has an infrared band [2] at frequencies accessible to the carbon dioxide infrared laser. The pyrolysis of alkyl-germanes is also known to give polycrystalline films of germanium almost free from carbon [12–16].

Recently, in the course of investigating a laser-induced, selective nitration process, several interesting phenomena were observed [17–19] involving the use of sulfur hexafluoride as a sensitizer for infrared, laser sensitized processes even when the material being used does have an absorption band which is accessible by the output frequency of the laser in use, for example, the carbon dioxide infrared laser. It was

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concluded that more of the sensitizer is not necessarily better. Our studies have clearly shown that not only is there an optimal quantity of sulfur hexafluoride but there is also an optimal excitation frequency which is required for the maximization of the selective product yield. It is possible that the prudent use of a sensitizer such as sulfur hexafluoride could also be beneficial in the production of high yield and high purity germanium using laser sensitized photochemistry.

Obviously, chemical reactions occur in a series of coupled chemical reactions which may be consecutive, parallel, or reversible [20,21]. The time dependence of such reactions is typically calculated by solving a number of coupled differential equations. The traditional approach is based on the deterministic formulation of chemical kinetics in which the reaction constants are considered reaction rates and the concentrations are considered to be continuous, single-valued functions of time. This approach assumes that the time evolution of a chemical species is continuous and deterministic. In reality, the time evolution of a chemically reacting system is neither continuous nor deterministic. Obviously, the molecular population levels can only change by discrete integer amounts. In many cases this assumption is not valid and cannot be taken for granted [21].

However, a systematic, computer-oriented procedure has been developed which uses a simple, compact, and efficient algorithm that imposes no approximations of the stochastic formulation of chemical kinetics. This approach, which appeared and is discussed in a number of publications [22–24], is particularly suggested for the investigation of laser photochemical phenomena. This stochastic formulation will be utilized to analyze the suggested reaction mechanism for the laser sensitized dissociation of tetramethyl germane.

The rate of depletion and formation data will be utilized in a simulation algorithm which was based on Gillespie's method [2w1,22–24] of stochastic time evolution of coupled chemical reactions. Gillespie's method [21,22–24] is based on a random number generator which simulates chemical reactions at increasing reaction times and defined concentrations of the reactants. The experimental data will be analyzed so that the algorithm will predict the outcome of the reactions that took place during irradiation. The proposed reaction mechanism will be supported by this described fitting using simulation analysis.

2. Materials and experimental details

2.1. Materials

Tetramethyl germane was obtained commercially from the Aldrich Chemical Co. The sulfur hexafluoride was obtained from Matheson Gas Products. Purity of the samples was monitored by a comparison of the gas phase infrared spectra to known spectra [25] and by injection into the gas chromatographic system described below. No purification was deemed necessary.

2.2. Infrared absorption measurements

The infrared spectra were recorded on a Mattson Sirius 100 interferometer equipped with a nitrogen purged bench, a deuterated triglycine sulfate detector, and a potassium bromide beam splitter. The effective resolution was 1 cm^{-1}. Ten scans were taken for each sample and for reference. A medium apodization function was used. The Beer's law relationships were determined and utilized for both sulfur hexafluoride, tetramethyl germane, and all identified gaseous products at several different wavelengths. At all times the average of three runs was used. The reliability of this technique was evaluated statistically.

2.3. Chromatographic measurements

The separation and analysis of all reaction mixtures were accomplished using a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a gas sampling loop and interfaced to an HP 5970 series mass selective detector. The chromatographic column was an HP Ultra 2 (cross linked 5% phenol methyl silicone) of about 40 m length, having a 0.2-mm interior diameter and 0.22 μm film thickness. The volumetric flow rate was 1.6 cm^3 min^{-1} (the linear flow rate was 10 m min^{-1}); the split ratio was 47:1; and the column head pressure was 10 psi. For chromatographic analysis of the reaction mixture, the initial oven temperature was ambient with no programming. Identification of the components of the chromatographic peaks was attempted using the computer search routine and the NBS43k Mass Spectra Library. Whenever possible, component identities were verified by a comparison with the gas chromatographic retention times and the mass spectra to those of known samples. The separation of all the components was possible with the chromatographic conditions used. The reliability of this method was evaluated statistically. At all times the average of three runs was used, as were standard curves prepared using the known compounds.

2.4. General irradiation procedures

Sample handling was accomplished using high standard vacuum line techniques. The gas phase irradiations were carried out in stainless steel cells (5 × 10 cm^2) equipped with O-ring seals [26] for securing the windows (5 cm diameter) onto the cells. The infrared laser beam entered through the zinc selenide windows at either end of the cell (traversing a 10 cm path). Potassium chloride windows were used on the short path length (traversing a 5 cm path) for recording the infrared spectra.

All irradiations followed the same general procedure. At all times the average of three runs was used. The initial sample pressures were measured with a MKS Baratron electronic manometer, consisting of a Type 222B transducer and a Type PDR-5B power supply digital readout. Infrared spectra of the gas mixtures before and after irradiation were obtained using the Mattson Sirius 100 Fourier transform infrared spectrometer described above. The sample pressures were varied, as was the ratio of sensitizer to reactant.

The Coherent Radiation model 41 continuous wave, carbon dioxide, tunable laser which provided the energy to drive the reactions was operated in a single mode at various selected wavelengths and powers as required for the specific experiment. The wavelength was verified with an Optical Engineering carbon dioxide spectrum analyzer. The powers were measured by a Coherent Radiation model 213 water-cooled power meter, and were varied experimentally.

The reaction cell was positioned on a movable stage which could be translated along the path of the laser beam. All samples were irradiated with the cell positioned behind the focal point where the beam was slightly diverging. The zinc selenide window allowed a beam transmittance of about 70% through to the sample. The reported laser powers do not correct for this window absorption, nor for the difference in the beam diameter at the sample, as opposed to the diameter at the power meter when the beam is larger. The beam diameter was approximately 2 mm at the point of entry into the reaction cell.

2.5. *Method of calculation*

The original algorithm written by Gillespie [21–24] is in FORTRAN, and is for one specific sequence of reactions. GW BASIC was the language used in a similar algorithm. This algorithm works for almost any sequence of reactions up to the maximum capacity of the computer memory. All random number generators were seeded as required, and evaluated to determine whether each generated a uniformly random distribution, as required. The algorithm was run on a Wyse PC, an IBM compatible with a 80 MB hard disk and 654 KB memory.

The simulation analysis consists of an algorithm which fits the simulated concentrations to the experimentally observed concentrations at a selected time. The rate constants are obtained from the simulation analyses and are modified to fit any number of experimental concentrations to a specified degree of fit. As usual for simulations, cycles must be run and averaged until the variance of the concentrations no longer decreases. It is well known that thirty cycles are mandatory to get statistically significant averages for the concentrations of the reactants and the products as a function of time.

3. Experimental results and discussion

The infrared spectrum of tetramethyl germane does not contain any infrared absorption bands between 900–1100 cm^{-1}. This necessitates the utilization of laser sensitized photochemistry to force the dissociation of tetramethyl germane. The infrared spectrum of a mixture of tetramethyl germane and sulfur hexafluoride is shown in Fig. 1(a). Sulfur hexafluoride is present to act as an infrared sensitizer which absorbs energy from the laser and redistributes the collisional energy to the tetramethyl germane which then decomposes. Typical experiments involved recording the infrared spectra of sulfur hexafluoride and tetramethyl germane using the infrared technique described above.

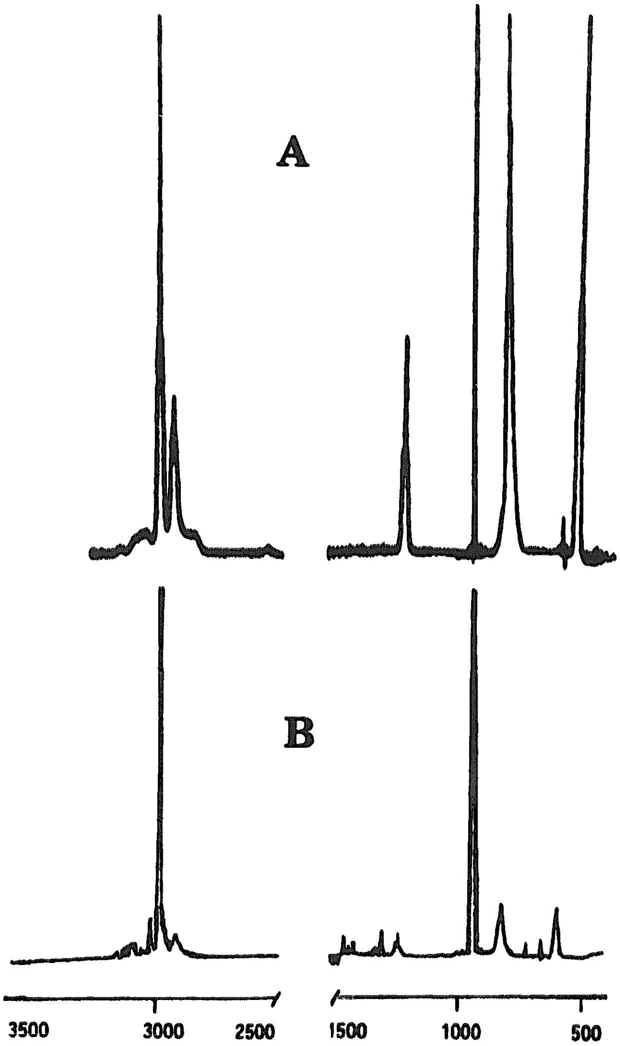
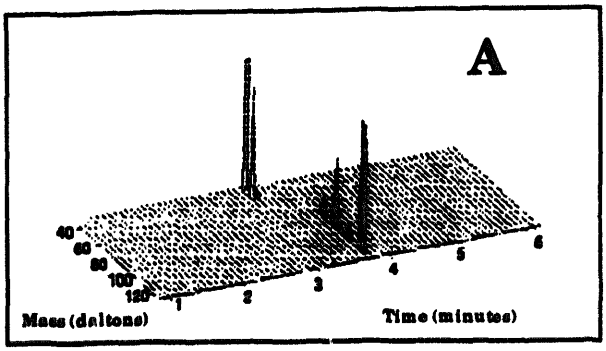


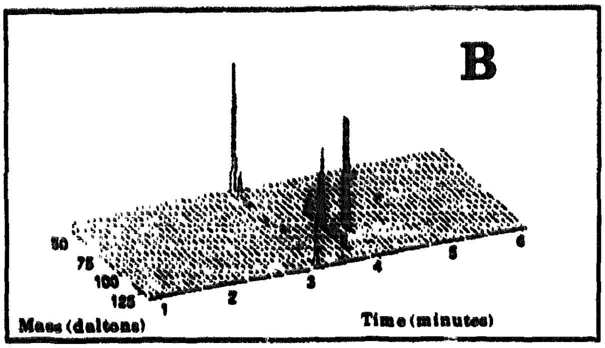
Fig. 1. Infrared spectra of the laser sensitized dissociation of tetramethyl germane using sulfur hexafluoride: (a) tetramethyl germane, 30.0 Torr, and sulfur hexafluoride, 0.4 Torr; and (b) product mixture after irradiation for 1 s at P(18) of (00°1)–10°0), 946 cm^{-1}, 100 W cm^{-2}.

3.1. *Tetramethyl germane*

A wide variety of mixtures of sulfur hexafluoride and tetramethyl germane were prepared and irradiated over a wide range of conditions. Figs. 1(a) and (b) show the infrared spectra of a typical mixture of sulfur hexafluoride and tetramethyl germane before and after irradiation. The Beer's law absorptivities were determined and used for tetramethyl germane at 2916 cm^{-1} and 1240 cm^{-1} and also for sulfur hexafluoride at 612 cm^{-1}. Beer's law absorptivities were also determined and used for all identified gaseous products using known compounds and appropriate absorption bands.



Time 0.83 to 6.12 min
Mass 30 to 127 daltons



Time 0.83 to 6.12 min
Mass 30 to 134 daltons

Fig. 2. Gas chromatographic/mass spectra of the laser sensitized dissociation of tetramethyl germane using sulfur hexafluoride. (a) Tetramethyl germane, 31.1 Torr, and sulfur hexafluoride, 0.3 Torr; and (b) product mixture after irradiation for 1 s at P(18) of (00°1)–(10°0), 946 cm^{-1}, 100 W cm^{-2}.

Sulfur hexafluoride is present to act as an infrared sensitizer which absorbs energy from the laser and redistributes the collisional energy to the tetramethyl germane which then decomposes. The energy associated with these reactions was also emitted as both light and heat. The gray solid on the interior of the cell confirmed the presence of germanium. The products that were formed by repeatedly irradiating the samples of tetramethyl germane and sulfur hexafluoride included methane, ethene, and ethyne. The concentration of all reactants and products except germanium and hydrogen was closely monitored, including sulfur hexafluoride which did not change in concentration at any time as a result of the irradiations.

Samples of tetramethyl germane and sulfur hexafluoride mixtures were also injected into the Hewlett Packard Model 5890/5970 gas chromatograph/mass spectrometer and analyzed both before and after irradiation. Figs. 2(a) and (b) show a typical gas chromatogram of a mixture of sulfur hexafluoride and tetramethyl germane before and after irradiation. The mass and infrared spectra, including the group frequencies [25,27–29], were also used to identify the gaseous products formed and the concentrations of the products. As stated, repetitive experiments were performed.

As shown by the gas chromatography/mass spectral analysis the gaseous products that were formed by repeatedly irradiating the samples of tetramethyl germane and sulfur hexafluoride included methane, ethene, and ethyne. The concentration of all the reactants and products except germanium and hydrogen was closely monitored using gas chromatograph/mass spectral techniques, including sulfur hexafluoride which did not change in concentration at any time as a result of the irradiations.

3.2. Laser sensitizer optimization

A variety of mixtures of sulfur hexafluoride and tetramethyl germane were prepared and irradiated over a very specific range of conditions. These experiments varied in sample pressure, the ratio of the pressures of sulfur hexafluoride to tetramethyl germane, laser power, and irradiation time. The different experiments were designed and used to both determine the optimum rate of decomposition and the best ratio of sensitizer to reactant for the maximum yield of germanium as stoichiometrically related to reactant depletion. Analysis using both techniques was combined for these optimization trials.

Initially, tetramethyl germane pressures were varied from approximately two torr to the vapor pressure of tetramethyl germane. Simultaneously, the sulfur hexafluoride was varied from a sample pressure of 0.2–5.5 torr. These samples were irradiated at a constant time (1 s), and a constant laser power (50 W cm^2) using the laser output frequency described below. Fig. 3 shows the optimization of the ratio of sensitizer pressure to the sample pressures. The optimal ratio obtained from that series of experiments is 0.8 torr of sulfur hexafluoride to 30.0 torr of tetramethyl germane.

The power was varied using the optimal ratio of sensitizer to reactant. The time was held constant at 1 s. As shown in Fig. 4, the power was varied from 25–100 W cm^{-2} in separate experiments. In this and some other laser sensitized processes,

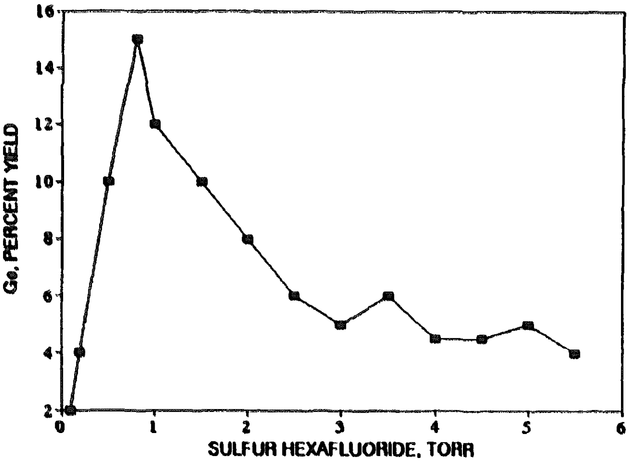


Fig. 3. Dependence of the yield of germanium on sensitizer pressure. Irradiations used 30.0 Torr of tetramethyl germane, 1 s irradiation time, and 50 W cm^{-2} at P(18) of (00°1)–(10°0), 946 cm^{-1}.

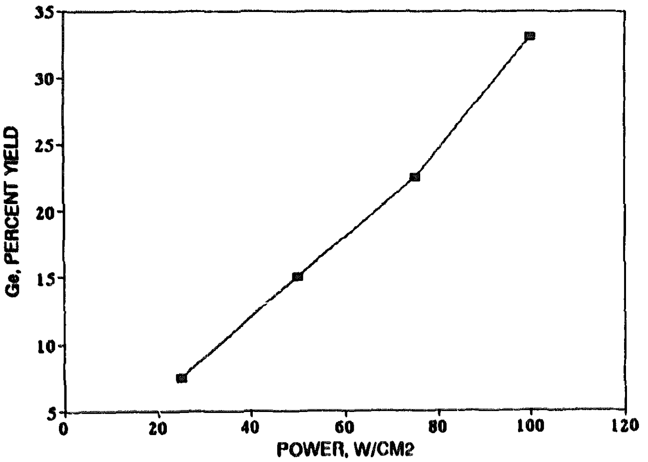


Fig. 4. Dependence of the yield of germanium on laser power. Irradiations used a sensitizer to reactant ratio of 0.8/30.0 Torr, 1 s irradiation and variable powers at P(18) of (00°1)–(10°0), 946 cm^{-1}.

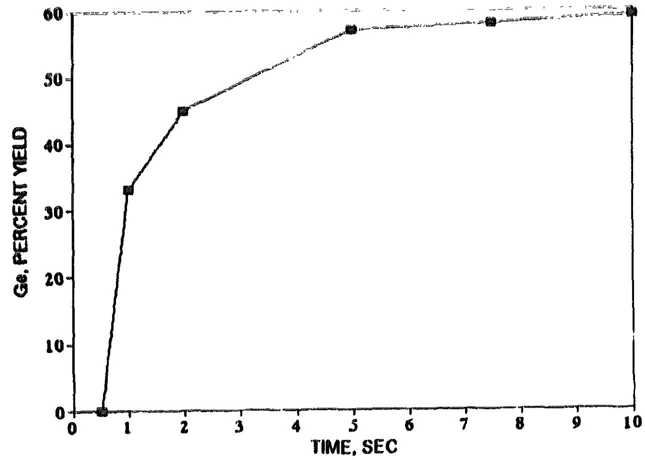


Fig. 5. Dependence of the yield of germanium on irradiation time. Irradiations used a sensitizer to reactant ratio of 0.8/30.0 Torr, variable times, and a power of 100 W cm^{-2}, at P(18) of (00°1)–(10°0), 946 cm^{-1}.

the higher the power, the higher the yield of product, specifically, germanium. The optimal laser power was 100 W cm^{-2}.

Separately, using those optimized conditions, the time was varied in discrete steps from 0.1–10.0 s at P(18) of (00°1)–(10°0), 946 cm^{-1}, 100 W cm^{-2}. As shown in Fig. 5, there is a reaction threshold time at one s. The yield increases and then levels off after 5 s of irradiation time. The percent yield of germanium obtained was 33% and 57% at 2 and 5 s irradiation time, respectively, at what is felt to be optimized experimental conditions.

3.3. Simulation analysis

The experimental data at both 1 and 5 s of irradiations was evaluated and the initial rates of the depletion and the reaction constants were estimated for use in the simulation analysis. Several reaction mechanisms were suggested and proven unsucessfully by lack of fit to the experimental data. Unsuccessful means that the simulation analysis was applied and the reaction mechanisms did not fit to the experimental data. Therefore these mechanisms were excluded.

Table 1
Reaction mechanism and rate constants

Reaction	c [a]
$(CH_3)_4Ge \rightarrow (CH_3)_3Ge^{\bullet} + CH_3^{\bullet}$	0.4196
$(CH_3)_3Ge^{\bullet} \rightarrow (CH_3)_2Ge^{\bullet} + CH_3^{\bullet}$	12.97
$(CH_3)_2Ge^{\bullet} \rightarrow (CH_3)Ge^{\bullet} + CH_3^{\bullet}$	13.72
$(CH_3)Ge^{\bullet} \rightarrow Ge + CH_3^{\bullet}$	14.85
$2CH_3^{\bullet} \rightarrow C_2H_4 + 2H^{\bullet}$	32.80
$2CH_3^{\bullet} \rightarrow C_2H_2 + 4H^{\bullet}$	0.2842
$CH_3^{\bullet} + H^{\bullet} \rightarrow CH_4$	20.95
$2H^{\bullet} \rightarrow H_2$	6.370

[a] Obtained from simulation analysis of fit to 10% of experimental data using four different measured concentrations.

The specific reaction mechanism which fit is similar to that suggested in the pyrolytic decomposition [30–32] and is listed in Table 1. Of the mechanisms tried, only this reaction mechanism fit. The experimental results were simulated and finally fit to within ten percent of experimental quantities which included the reactant and three products. The reaction rate constants obtained from the simulation analysis are listed in Table 1. The simulated concentrations of tetramethyl germane and all products as a function of time are shown in Figs. 6(a), (b) and (c), along with the experimental results which were utilized originally to estimate and fit.

4. Conclusion

Using both infrared spectral and gas chromatographic/mass spectral techniques, the products that were formed by repeated irradiation of the samples of tetramethyl germane and sulfur hexafluoride included methane, ethene and ethyne. Germanium was also presented as a product at all times observed in the form of a gray solid in the cell.

Mixtures of sulfur hexafluoride and tetramethyl germane were prepared and irradiated over a very specific range of conditions. These experiments varied in sample pressure, the ratio of the pressures of sulfur hexafluoride to tetramethyl germane, laser power, and irradiation time. These different experiments were designed and used to both determine the optimum rate of decomposition and the best ratio of sensitizer to reactant for a maximum yield of germanium. Analysis using both techniques was combined for these optimization trials. Concentrations were computed using Beer's law relationships and standard gas chromatographic curves.

The irradiation of tetramethyl germane showed how the variation in pressures, irradiation times, laser powers, and the use of a sensitizer can have an impact on the depletion rates. Experimentally higher pressures for the reactant gave higher yields. This is beneficial if higher yields of germanium are needed. A variation in the laser power can also increase the rate of depletion by providing the mixture with more energy,

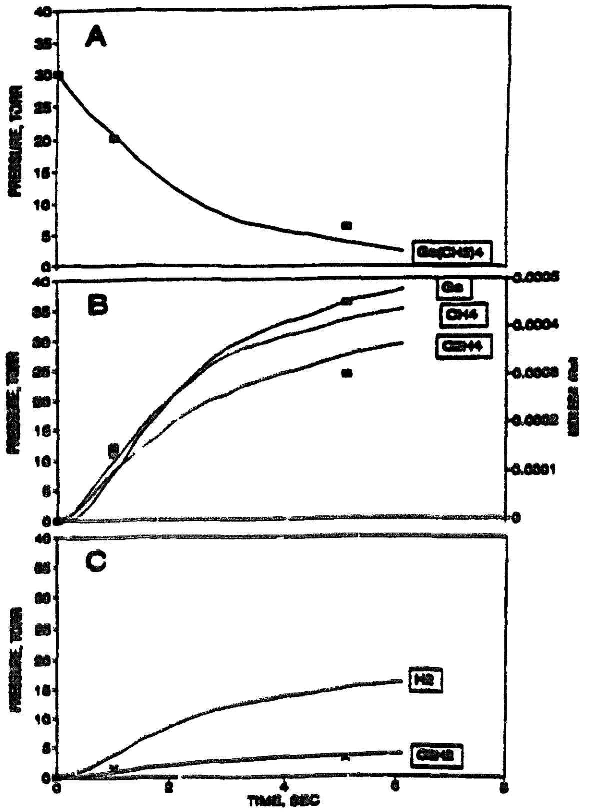


Fig. 6. Average experimental and simulated concentration versus time data for the dissociation of tetramethyl germane into products: (a) Average depletion of tetramethyl germane as a function of time. The line shows the simulated results. Experimental data is shown by filled squares; (b) average formation of germanium, methane, and ethene as a function of time. The lines show the simulated results. Experimental data for methane and ethene is shown by open boxes and boxes with an X, respectively; and (c) average formation of ethyne and hydrogen as a function of time. The lines show the simulated results. Experimental data for ethyne is shown by X's.

which is effectively a higher temperature. Variation in the irradiation times clearly showed that there is a reaction threshold at one s. Although longer irradiation times increases the rate of depletion, most of the dissociation of tetramethyl germane takes place in 5 s, as is supported by the simulation analysis. The highest experimental yield was achieved using, specifically, the mixture of 0.8 torr of sulfur hexafluoride with 30.0–31.0 torr of tetramethyl germane at 5 s irradiation time and 100 W cm^{-2} at the already described output line. The percentage yield of germanium was 33% and 57% at 1 and 5 s irradiation time, respectively.

Numerous reaction mechanisms were considered, with the best and only simulation analysis fit being the one which is identical to that suggested in a pyrolytic study [30] of tetramethyl germane. The reaction mechanism used to simulate the reaction rates obtained from our fit to experimental data is given in Table 1. Experimental and simulated results are shown in Fig. 6. The simulation analysis conclusion is very similar to those conclusions from the kinetic study of tetramethyl germane done by stock tube analysis [33]. Simulation analysis implies, as stated, statistically significant averages and statistically significant fitting. The fact that these reaction mechanisms fit does not mean that other reaction mechanisms might not only fit, but be a better explanation than what is used here.

These results, both experimental and simulated, compare favorably with the results reported in the kinetic studies [30–32] of the pyrolysis. The pyrolysis study reported the production of predominantly methane, 90.5%, with ethane and hydrogen present in approximately equal quantities under certain conditions. Their kinetic relationships [30–32] were assumed to be accurate and were used to calculate the reaction temperatures for the laser sensitized photochemical dissociation of tetramethyl germane. These calculated temperatures ranged from 798–818 K, which is a good estimation of the temperatures of these laser sensitized processes. It is a similar to the effective beam temperatures reported in a similar study of the laser-induced dissociation of germane [34].

Simulation analysis based on D.T. Gillespie's theory was used successfully to determine simulated concentrations that are accurate to within ten percent or better for four different substances: one reactant and three products. Simulation analysis also was used successfully to evaluate and support the choice of a reaction mechanism to a high degree of accuracy using fit to experimental data, to exclude some mechanisms.

References

[1] A.E. Stanley, R.A. Johnson, J.B. Turner and A.H. Roberts, *Appl. Spectrosc.*, *40* (1986) 374.
[2] A. Stanley, *US Patent No. 4 681 640* (1986).
[3] C.G. Devyatykh, Yu.A. Nechllneev and A.S. Yushin, *Zh. Neorg. Khim.*, *23* (1978) 1447.
[4] G.G. Devyatykh and Trudy po Khim, *I. Kim. Tekhnol. (Goikii)*, *2* (1962) 221.
[5] *US Patent No. 3147141 Cl.118-49.1* (1964).
[6] *US Patent No. 3 112997 Cl.23-223.5* (1963).
[7] *BRD P. No. 1170912 Cl.12, 13/00* (1964).
[8] *British Patent No. 883800* (1961).
[9] *British Patent No. 1345890* (1972).
[10] *British Patent No. 1822347* (1973).
[11] R.W. Andreatta, C.C. Abler, J.F. Osmundsen, J.G. Eden, D. Lubber and J.I. Greene, *Appl. Phys. Lett.*, *4* (1) (1982) 183.
[12] H.W. Kattenberg, W. Cubes and A. Oskam, *J. Mol. Spectrosc.*, *44* (1972) 425.
[13] V.A. Yablokov, A.V. Dvyorov, I.A. Feschenko and A.D. Zorin, *Zh. Obsh. khi*, *53* (1) (1983) 126.
[14] G.A. Razuvalv, G.A. Domrachev, V.S. Kaverin, K.G. Kochetikhina and B.A. Nesterov, *Dokl. Akad. Nauk. USSR*, *188* (1969) 1607.
[15] Y. Avigal, D. Itzhak and M. Schieber, *J. Electrochem. Soc.*, *122* (1975) 1226.
[16] C.P. Smith and R. Patrick, *Int. J. of Chem. Kinet.*, *15* (1983) 167.
[17] A.E. Stanley, S.E. Godbey, J.M. Bonicamp and L.M. Ludwick, *Spectrochim. Acta* *49A* (1993) 1987.
[18] A.E. Stanley, S.E. Godbey and L.M. Ludwick, *U.S. Army Missile Command Technical Report TR-RD-WS-93-1*, Redstone Arsenal, AL (1993).
[19] A.E. Stanley, L.M. Ludwick, D. White, D.E. Andrew and S.E. Godbey, *Appl. Spectrosc.*, *46* (1992) 1866.

[20] S.W. Benson, *The Foundation of Chemical Kinetics*, McGraw-Hill, New York, 1960, p. 346.

[21] D.T. Gillespie. Markov Processes: *An Introduction for Physical Scientists*, Academic Press, 1991.

[22] D.T. Gillespie, *J. Comp. Phys.*, *22* (1976) 401–434.

[23] D.T. Gillespie, *J. Phys. Chem.*, *81* (1977) 2340–2361.

[24] D.T. Gillespie, *J. Stat. Phys.*, *16* (1978) 311–318.

[25] E.R. Lippincott and M.C. Tobin, *J. Am. Chem. Soc.*, *75* (1953) 4141.

[26] A.E. Stanley and R.T. Grimly, *Appl. Spectrosc.*, *42* (1) (1988) 181.

[27] G. Herzberg, *Infrared and Raman Spectra*, Van Nostrand Reinhold, New York, 1945.

[28] G. Herzberg, *The Spectra of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1935.

[29] D.S. Erley and B.N. Blake, *Infrared Spectra of Gases and Vapor*, Vol. II, DOW Chemical Co., Midland, MI, 1965.

[30] J.E. Taylor and T.S. Milazzo, *J. Phys. Chem.*, *82* (1978) 847.

[31] R.L. Geddes and E. Marks, *J. Am. Chem. Soc.*, *52* (1932) 4372.

[32] G.P. Smith and R. Patrick, *Int. J. of Chem. Kinet.*, *15* (1983) 167–185.

[33] J. Dzarnoski, M.A. Ring and H.E. O'Neal, *Int. J. of Chem. Kinet.*, *14* (1982) 279.

[34] A.E. Stanley, *Appl. Spectrosc.*, unpublished results.