

SiF₄-Sensitized Decomposition of GeH₄ by a Pulsed CO₂ TEA Laser^{1,2}

J. Błażejowski[†] and F. W. Lampe*

Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802 (Received: July 19, 1988; In Final Form: June 5, 1989)

The decomposition of GeH₄, sensitized by multiphoton absorption of unfocused infrared laser radiation by SiF₄, has been studied in the fluence range 0.2–0.9 J/cm² and over a total pressure range of 1–70 Torr. Strong absorption of energy from a pulsed CO₂ laser photon field (P40 line; 1027.4 cm⁻¹) and subsequent energy-transfer processes cause an increase in the temperature of the system. As a result of these processes, decomposition of GeH₄ occurs leading to the formation of stoichiometric amounts of metallic germanium and molecular hydrogen. The effects of initial composition, pressure, fluence, and presence of foreign gases (He, H₂) on the yield of GeH₄ decomposition were examined. A reaction model is proposed which assumes that molecules initially present in the absorption volume are heated by the laser pulse and subsequently decompose unimolecularly. Since the decomposition process is exothermic, it prompts a further increase in temperature and thus enhances the decomposition process. Both absorption and decomposition create a shock wave causing expansion of hot gas into cool surrounding volume. The latter process brings about cooling of the hot gas and quenches the decomposition process. Taking into account the above-mentioned effects the temperature profiles (*T* versus time and geometry of the reaction zone) were evaluated on the basis of statistical thermodynamics, assuming that, at any stage, the system attains thermal equilibrium. Yields of decomposition were then derived with *k*_{uni} values calculated by the RRKM method. The proposed approach accounts satisfactorily for the experimentally observed dependencies, and we believe it can be generally applied to the description of photosensitized processes in the infrared region.

Introduction

Since the discovery in the early 1970s^{3,4} that the intense CO₂ laser photon field can initiate chemical changes in irradiated systems, many aspects regarding this phenomenon have been examined. A considerable number of reports in this field have revealed that the mechanism of the photon absorption generally depends on the intensity of the infrared laser radiation. At moderate fluences (parallel beam), efficient absorption requires that rotational–vibrational transitions in the compound match closely the frequencies of photons emitted by the CO₂ laser.^{5–7} Under such conditions the amount of energy absorbed can be expressed by phenomenological relationships,^{2,6–9} some of which admit modified forms of the Lambert–Beer equation.^{2,6,7,9} At higher fluences (focused beam), however, the energy can virtually be absorbed by any system and the process has the nature of a dielectric breakdown.^{10–13}

A low-resolution absorption spectrum of natural germane (Figure 1) reveals the weak absorption of infrared radiation in the emission region of the CO₂ laser. Careful analysis of the high-resolution IR spectrum of GeH₄ demonstrates, however, that none of the rotational–vibrational transitions in the compound^{14,15} match the frequencies emitted by the CO₂ laser.⁵ Direct measurements performed in our laboratory confirm that natural germane is transparent to pulsed CO₂ laser radiation of parallel geometry,⁷ and therefore, the infrared photochemistry of GeH₄ cannot be studied directly with this type of laser. The aim of this work was to examine the behavior of the compound in the infrared region, in the presence of SiF₄ as a sensitizer. SiF₄ is, in our opinion, the best among proposed infrared photosensitizers. The triply degenerate vibrational transition (*ν*₃), centered at 1030.9 cm⁻¹, occurs in the emission region of a CO₂ laser.^{5,9,16} Moreover, the compound remains chemically inert in an intense IR laser field owing to the relatively high Si–F bond dissociation energy,¹⁷ is unreactive in the presence of GeH₄, is easy to work with, and is commonly available.

The behavior of chemical systems irradiated with infrared lasers in the presence of sensitizers is still not well-understood. At the present time, two points of view are prevalent. According to one of them, energy absorption by a sensitizer is followed by fast V–V,R,T energy transfer, i.e., as a result, fast thermalization takes place. Therefore, the absorption of energy from the laser photon field simply causes heating of the system, and the resulting

chemical changes can be considered as a category of thermal processes.^{18–21} Another approach is based on the assumption that energy transfer proceeds predominantly via V–V energy transfer and that the system does not attain thermal equilibrium before decomposition of molecules is initiated.^{22,23} The rate of decomposition can, in this case, be controlled by the rate of V–V energy transfer from the sensitizer to reactant molecules.²² In this work we have made a successful attempt to describe the SiF₄-sensitized decomposition of GeH₄ by a model assuming thermalization of the system during and immediately after the pulse of radiation.

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[†] Permanent address: Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland.

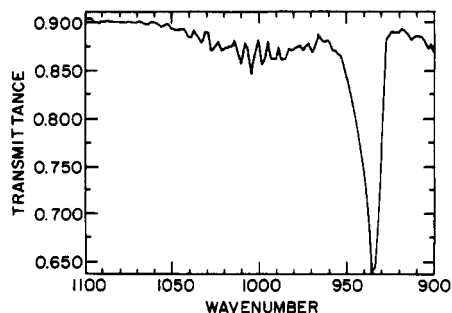


Figure 1. Low-resolution IR absorption spectrum of natural GeH₄ at pressure of 30 Torr and optical path length of 11.5 cm (recorded on an IBM IR/32 spectrometer).

Various aspects regarding the infrared photodecomposition of PH₃^{12,16,25} and SiH₄²⁵⁻²⁹ have been examined previously in our laboratory, and in this work we extend the investigations to GeH₄, a molecule which shows many similarities to SiH₄. Several aspects of the photochemistry³⁰⁻³⁴ and thermochemistry³⁵⁻⁴⁴ of natural germane have been examined in the past. However, knowledge of the infrared photodecomposition of GeH₄ is rather scattered and fragmentary. GeH₄ and its ethyl-substituted derivatives decompose in a focused CO₂ laser beam forming Ge polycrystalline films.⁴⁵ Depletion of GeH₄ has been also observed upon irradiation of SiH₄-GeH₄ mixtures with a parallel pulsed CO₂ laser beam.⁴⁶ This process is, however, initiated by the insertion reaction of SiH₂ into GeH₄, rather than by direct decomposition of germane. To our knowledge, excepting our preliminary report,² no other information regarding the SiF₄-sensitized decomposition of GeH₄, initiated by a CO₂ laser, has appeared.

It is perhaps worthwhile to mention some utilitarian aspects of this investigation. In the past few years there has been wide interest in the development of new methods for the preparation of photosensitive and semiconductive layers for various electronic devices. These layers are usually produced by the decomposition of silicon, germanium, phosphorus, or boron hydrides. Recently, considerable attention has been devoted to photochemical methods of deposition,^{47,48} and it is worth noting that studies regarding the application of these methods for the deposition of Ge-containing layers have already been undertaken.^{34,45,49,50} The use of infrared

sources for this purpose seems particularly promising. Since the process is initiated in the ground electronic state, only the thermodynamic or kinetic barrier for the decomposition is required to be surmounted and, thus, it is energetically efficient. Moreover, due to the expected selectivity of primary processes there exists a better chance to control the overall decomposition and deposition process. Hence, knowledge of the infrared photodecomposition of GeH₄ may be helpful in the development of new methods for the production of commercially interesting Ge-containing layers.

Lastly, since germane has been discovered in Jupiter,⁵¹ Saturn,⁵² and Uranus,⁵³ the present study may be of help in the elucidation of the chemistry of these planetary atmospheres.

Experimental Section

Apparatus. The source of infrared radiation was a pulsed CO₂ TEA laser (Lumonics Research Ltd., Model 103-2) tuned to the P40 line of the 00⁰1-02⁰0 transition (1027.4 cm⁻¹).⁵ The laser was operated in the single-pulse mode with lasing initiated at a constant voltage of 40 kV. These conditions assured relatively high replication of energy per pulse. The composition of the lasing gas was He:CO₂:N₂ = 6.0:2.0:0.7. The temporal distribution of the laser pulse was not investigated; however, on the basis of works of other authors⁵⁴⁻⁵⁶ a typical pulse of this laser consists of a spike of duration less than 150 ns followed by a tail decaying to zero intensity in ca. 3 μs. The irradiations were performed with an unfocused beam whose central portion, of area 3.5 cm², was separated by an iris. The fluence of the CO₂ laser pulses was controlled by passing the beam through sheets of polyethylene.

The irradiations were carried out in a cylindrical stainless steel cell that had an optical length of 15.5 cm and a volume of ca. 150 cm³. Both ends of the cell were equipped with sodium chloride windows, while transverse to the cylinder axis was a pinhole leak of approximately 20-μm diameter leading into the ionization region of a Bendix Model 14-101 time-of-flight mass spectrometer.²⁴ The amounts of incident pulse energy (E_0), the energy transmitted by the empty cell (E_{empty}), and energy transmitted by the cell filled with a reacting gas mixture (E_{full}) were measured by a Gen-Tec Model ED-500 joulemeter.

Materials. GeH₄ (99.99%), SiF₄ (99.99%), He (99.995%), H₂ (99.99%), and 1,3-butadiene (99.5%), all from Matheson, and ethylene (99.9%) from Phillips Petroleum Co. were used as received. All gas mixtures were prepared with a Saunders-Taylor apparatus.⁵⁷

Determination of the Extent of Reaction and Reaction Yields. The changes in concentrations of germane and H₂ during the photolyses were followed by measurements of the intensities of the ion currents at m/e 76 and 2 amu, respectively. The ion current at m/e 76 is the most abundant in the mass spectrum of natural germane^{58,59} and arises predominantly from ⁷⁴GeH₂⁺. Other species contributing to the ion current at m/e 76 are ⁷³GeH₃⁺ and ⁷⁶Ge⁺. Their contributions (in percent) are 15.0 and 7.9, respectively. Assuming that the process is not isotopically selective, the fraction of GeH₄ decomposed can be determined from the measurements of the depletion of any ion current arising from natural germane. The intensity at m/e 2 was corrected for a small contribution from GeH₄. The pertinent calibration con-

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stant, which relates current at $m/e = 2$ to the concentration of H_2 , was determined by using pure H_2 diluted with SiF_4 or rare gases. All quantitative experiments were performed at an ionizing energy of 50 eV.

To determine concentrations reliably, the fraction of GeH_4 decomposed had to be at least 0.15, and to achieve such a degree of conversion, exposure by more than one pulse usually was necessary. In this case the initial concentrations before each pulse decrease with the number of pulses (N). To handle the problem uniformly, we determined the values of initial rate of reaction, $R(-GeH_4)$, in terms of number of moles of GeH_4 depleted after irradiation by the first pulse. Let $n_0(GeH_4)$ and $n_N(GeH_4)$ be the initial (before the exposure) and final (after irradiation by N pulses) number of moles of substrate in the irradiation cell, respectively. Then an equation for $R(-GeH_4)$ can be derived,⁶⁰ assuming that decomposition of GeH_4 proceeds according to a unimolecular mechanism, viz.

$$R(-GeH_4) = n_0(GeH_4) \left\{ 1 - \left[\frac{n_N(GeH_4)}{n_0(GeH_4)} \right]^{1/N} \right\} \quad (1)$$

Analogously, the rate of H_2 formation is given by

$$R(H_2) = x n_0(GeH_4) \left\{ 1 - \left[1 - \frac{1}{x} \frac{n_N(H_2)}{n_0(GeH_4)} \right]^{1/N} \right\} \quad (2)$$

where x represents the number of moles of hydrogen liberated from 1 mol of germane and $n_N(H_2)$ denotes final amount of moles of hydrogen formed. The effect of the decrease of the gas pressure as a result of the diffusion through the pinhole leak is negligible under our experimental conditions.

Yields of reactions, in terms of moles of substrate decomposed or product formed per joule of absorbed energy, $Y(-GeH_4)$ or $Y(H_2)$, respectively, were evaluated by dividing appropriate values of $R(-GeH_4)$ or $R(H_2)$ by the amount of energy absorbed per pulse, as measured directly; $E_{abs} = (E_{full} - E_{empty})$.

RRKM Calculations. The pressure- and temperature-dependent unimolecular rate constants for the decomposition of GeH_4 were calculated by the RRKM method using the expression⁶¹ in (3), viz.

$$k_{uni}(T, P) = \frac{L^+}{N_0 h Q_v} \exp[-E_k/(RT)] \int_0^\infty \frac{P(E_v^+) \exp[-E_v^+/(RT)]}{1 + k_a(E)/(\sum_i \lambda_i z_i P_i)} dE_v^+ \quad (3)$$

Further, the energy-dependent rate constants, $k_a(E)$, were evaluated from the expression⁶¹ shown in (4), viz.

$$k_a(E) = \frac{L^+}{N_0 h Q_v} \frac{P(E_v^*)}{N(E_v^*)} \quad (4)$$

In both (3) and (4) the influence of rotations on the rate constants was neglected. N_0 , h , R , and T represent Avogadro's number, Planck's constant, the gas constant, and temperature, respectively. The vibrational partition function, Q_v , was evaluated by standard procedures.⁶¹ For the reaction-path degeneracy, L^+ , we took a value of 6, assuming a three-center elimination mechanism.²⁸ The critical energy (E_k) was taken to be 193 kJ/mol on the basis of the Arrhenius activation energy.^{44,62} The sums, $P(E_v^+)$, and densities, $N(E_v^*)$, of states were obtained by the Whitten-Rabinovitch approximation.⁶¹ In the latter evaluation the following frequencies for GeH_4 (in cm^{-1})⁴⁴ were used: ν_1 , 2106 (1); ν_2 , 931 (2); ν_3 , 2112 (3); and ν_4 , 819 (3), the degeneracies of the vibrations being indicated parenthetically. For the activated complex, one frequency at 2112 cm^{-1} was omitted while the remaining were taken to be identical with those for the GeH_4 molecule. We

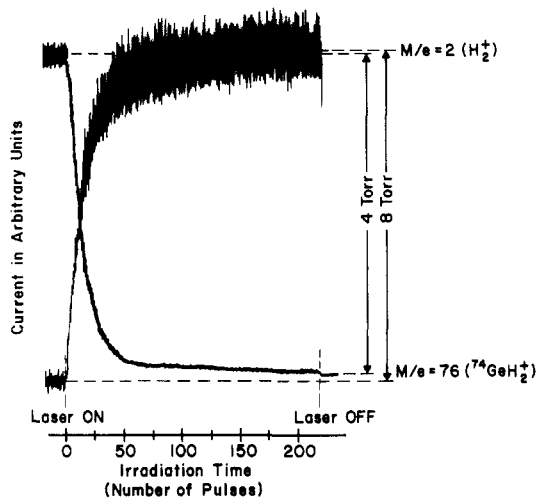


Figure 2. Photolysis of $[GeH_4]:[SiF_4] = 1:3$ mixture at a total pressure of 16 Torr and incident pulse energy of 1.8 J.

assumed that all components of the reactant mixture participate in the collisional deactivation. Thus, the collisional deactivation rate constant is written in (3) as a sum, $\sum_i \lambda_i z_i P_i$, where λ represents the efficiency of collisions, Z is the frequency of two-center collisions, and P denotes the pressure of a given component. λ was assumed to be equal to 1 for collisions of energized GeH_4 molecules with GeH_4 and SiF_4 (strong collision assumption). For GeH_4-He and GeH_4-H_2 a value of 0.25 was chosen arbitrarily.⁴³ Lastly, values of Z were calculated by using the following Lennard-Jones diameters (in 10^{-10} m):^{63,64} 2.6, 2.9, 4.1, and 6.3 for He, H_2 , GeH_4 , and SiF_4 , respectively.

Results

General Features of Photoinduced Decomposition. Examination of the overall mass spectra of the contents of the irradiation cell before and after the exposure revealed that the only gaseous product formed is molecular hydrogen. Moreover, material balances showed that decomposition of germane is accompanied always by the formation of two molecules of hydrogen per molecule of substrate (i.e., $x = 2$). The extent of the photoinduced decomposition was monitored by tracing ion currents corresponding to GeH_4 and H_2 as a function of time or, equivalently, as a function of the number of pulses. An example of changes in the concentration of reactant and product is shown in Figure 2. The curves for the depletion of germane and for the formation of hydrogen are almost mirror images. This reaction pattern is characteristic for any experimental conditions chosen and indicates that H_2 is released simultaneously with the decomposition of GeH_4 . Another characteristic feature is that, under certain experimental conditions, the decomposition of germane may be complete after irradiation by an adequately large number of pulses.

The photoinduced decomposition of germane is always accompanied by the formation of a solid product. Under the experimental conditions employed the solid appears as a poorly adherent microcrystalline deposit on the window and walls of the irradiation cell. As was mentioned earlier, the material balances indicate the absence of hydrogen in the solid products. To confirm this finding, the samples of solid deposits were subjected to IR and elemental analyses. Indeed, both methods excluded the presence of hydrogen in the solid.

Energy Absorption. The results of energy absorption experiments are shown as points in the lower graphs of Figures 3–6. As may be seen, the optical density, $\ln(E_{empty}/E_{full})$, depends on the incident pulse energy (Figures 4 and 5), total pressure (Figure 4), and the presence of foreign gases (Figure 6). All the absorption data clearly demonstrate that the Beer-Lambert law is not obeyed under the prevailing high-radiation-density conditions. Extended

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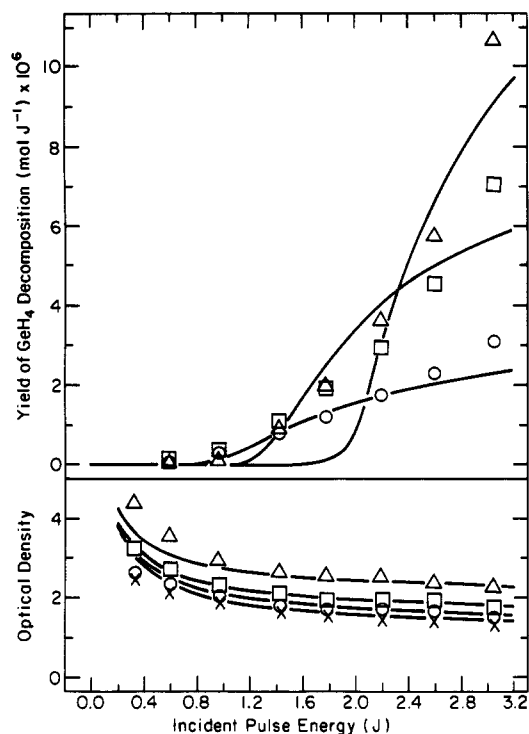


Figure 3. Dependence of the optical density (lower graph) and yield of GeH₄ decomposition (upper graph) on the incident pulse energy (pressure of SiF₄ = 6 Torr): (x), neat SiF₄; (o), [GeH₄]:[SiF₄] = 1:3 mixture; (□), [GeH₄]:[SiF₄] = 1:1 mixture; (Δ), [GeH₄]:[SiF₄] = 3:1 mixture.

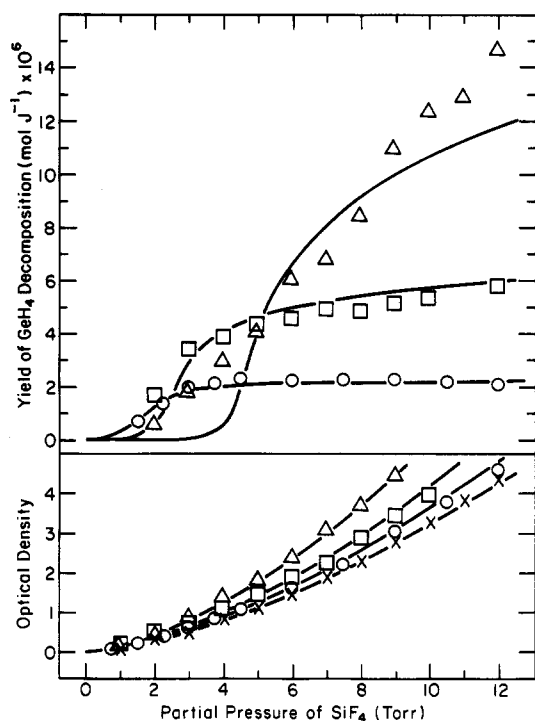


Figure 4. Optical density (lower graph) and yield of GeH₄ decomposition (upper graph) versus pressure of a reactant mixture ($E_0 = 2.6$ J/pulse): (x), neat SiF₄; (o), [GeH₄]:[SiF₄] = 1:3 mixture; (□), [GeH₄]:[SiF₄] = 1:1 mixture; (Δ), [GeH₄]:[SiF₄] = 3:1 mixture.

studies of the absorption of high-power CO₂ laser radiation revealed two characteristic features of this phenomenon.^{2,6-9} Firstly, the optical density of the system decreases with an increase of the intensity of radiation, showing saturation-type dependence. Secondly, the optical density of the system markedly increases with an increase in the number of absorbing and nonabsorbing molecules in the system. Undoubtedly, the latter effect results from the influence of collisions on the absorption process. Taking

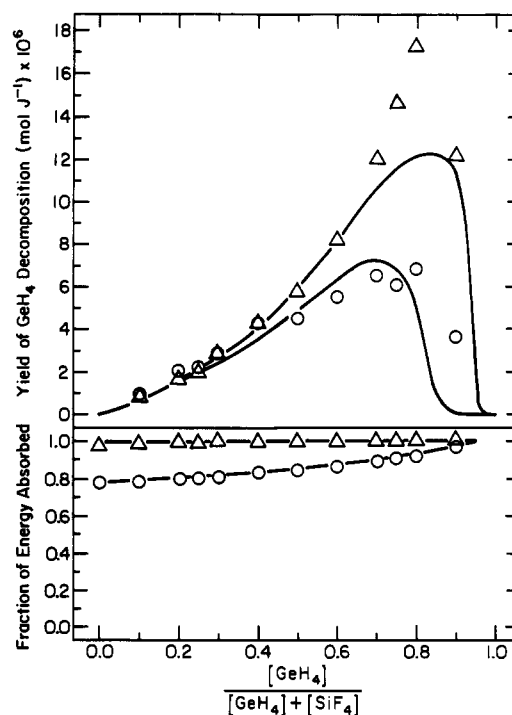


Figure 5. Fraction of energy absorbed (lower graph) and yield of GeH₄ decomposition (upper graph) versus composition of a reactant mixture ($E_0 = 2.6$ J/pulse): (o), $P(\text{SiF}_4) = 6$ Torr; (Δ), $P(\text{SiF}_4) = 12$ Torr.

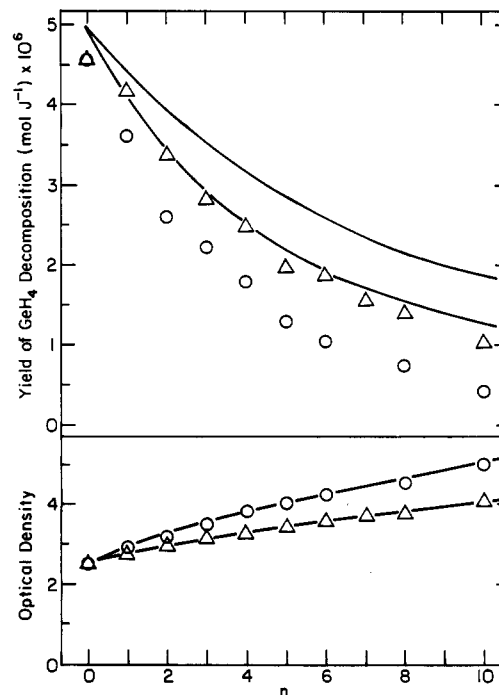


Figure 6. Optical density (lower graph) and yield of GeH₄ decomposition (upper graph) in the presence of foreign gases. $E_0 = 2.6$ J/pulse; $P(\text{SiF}_4) = 6$ Torr; [GeH₄]:[SiF₄]:[foreign gas] = 1:1:n; (Δ), $n = \text{He}$; (o), $n = \text{H}_2$.

into account the above-mentioned effects, we noticed earlier that the absorption of energy can be conveniently described by a phenomenological relationship that is a modified form of the Beer-Lambert law, viz.^{2,6,7}

$$OD = \epsilon_0 \frac{1 + [C_0 + C_1(P_1/P_0)^{m_1} + \sum_i C_i(P_i/P_0)^{m_i}](E_0/E_c)}{1 + E_0/E_c} lP_1 \quad (5)$$

where OD is the optical density of the system, P_1 , P_i , and P_0

represent the pressure of an absorbing gas (SiF_4), pressures of other components of the mixture, and standard pressure (atmospheric pressure), respectively, l is the optical path length, E_0 represents the incident pulse energy (J/pulse), and ϵ_0 , C_0 , C_1 , C_i , m_1 , m_i , and E_c are empirical constants.

It is worthwhile to point out a few characteristic features of this equation. Equation 5 presents a saturation-type relationship versus E_0 . Under low-radiation-density conditions ($E_0 \rightarrow 0$), it reduces to the form of the standard Beer-Lambert equation: $\text{OD} = \epsilon_0 l P_1$. Thus, ϵ_0 can be identified with a low signal absorption coefficient. In the limit of $\epsilon_0 \rightarrow \infty$, the optical density becomes independent of the pulse energy but depends on the composition of the absorbing system. The sum in the square brackets of (5) accounts for the effect of collisions on the absorption process; the second term represents this effect for absorbing molecules (SiF_4). The remaining terms describe the enhancement of absorption caused by other molecules present in the system (GeH_4 and bath molecules He and H_2).

We made an attempt to fit eq 5 to the experimental absorption data within the framework of the simplex optimization procedure.⁶⁵ The solid lines in the lower graphs of Figures 3-6, giving the best fit, correspond to the following values of constants: $\epsilon_0 = 0.075 \text{ cm}^{-1} \text{ Torr}^{-1}$, $E_c = 0.16 \text{ J/pulse}$, $C_0 = 0.047$, $C_1 = 8.1$, $C(\text{GeH}_4) = 2.1$, $C(\text{He}) = 1.6$, $C(\text{H}_2) = 2.7$, $m_1 = 0.87$, $m(\text{GeH}_4) = 0.75$, $m(\text{He}) = 0.76$, $m(\text{H}_2) = 0.77$.

Since terms in the square brackets of (5) may be considered as describing the effect of collisions on the absorption process, they should be proportional to the number of two-center collisions, and consequently pressures, of colliding molecules. If each collision affected the absorption of energy, m_1 and m_i values would be equal to 1. Examination of the values of the constants indicates that m_1 and m_i are always lower than 1, and this suggests that the efficiency of collisional energy enhancement is lower than 1, i.e., not each collision affects the absorption process. Similar regularities have been found earlier.^{6,7}

Equation 5 was found on a purely phenomenological basis. Nevertheless, it explains several physical effects accompanying the multiphoton absorption process and, moreover, presents very useful and simple formulas for the calculation of the amount of energy absorbed under given experimental conditions.

Reaction Yields. The extent of reaction in this work is reported in terms of reaction yields, quantities defined in the Experimental Section. Since under any experimental conditions obtaining, $Y(-\text{GeH}_4) = 1/2 Y(\text{H}_2)$, it is sufficient to present only the yields of decomposition of GeH_4 . The dependence of experimental $Y(-\text{GeH}_4)$ on the incident pulse energy, total pressure, composition of the reactant mixture, and the presence of foreign gases is presented as points on the upper graphs of Figures 3-6. Figures 3 and 4 demonstrate the threshold nature of the SiF_4 -photosensitized decomposition of germane. GeH_4 begins to decompose at a fluence equal to ca. 0.3 J/cm^2 . The extent of decomposition increases markedly when the fluence is increased above the threshold value (Figure 3). The pressure threshold for the decomposition is, however, less pronounced (Figure 4). The dependence of reaction yield on the composition of the reactant mixture is typical for two-component systems (Figure 5). It may be noticed that at a constant pressure of SiF_4 the yield of GeH_4 decomposition attains maximum values at a $[\text{GeH}_4]:[\text{SiF}_4]$ ratio equal to ca. 4:1. The decomposition yield decreases markedly in the presence of foreign gases as may be seen in Figure 6. Similar dependencies to those shown in Figures 3-6 have been observed in the SiF_4 -photosensitized decomposition of SiH_4 ,^{25,27} PH_3 ,^{16,25} and other compounds.

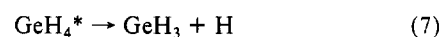
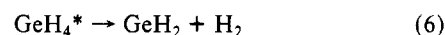
Discussion

Features of the Energy Deposition. SiF_4 molecules are the only species in the systems examined that interact with the CO_2 laser photon field. The energy absorption and redistribution processes occur in a very short time compared to the duration of the laser pulse. Thus, the molecules of sensitizer will gain energy essentially

instantaneously during the pulse. It may be assumed that the energy deposited is redistributed randomly between the various vibrational degrees of freedom of the sensitizer molecule. The excited SiF_4 molecules will tend to transfer energy to the molecules of their environment. Knowledge of the time scale for these processes requires information on the kinetics of the $\text{V}(\text{SiF}_4) \rightarrow \text{V,R,T}(\text{GeH}_4, \text{bath molecules})$ energy exchange, but unfortunately, such data are not available for the systems studied. General knowledge of energy-transfer phenomena suggests that collisional exchange of vibrational energy between SiF_4 and GeH_4 molecules should be very efficient⁶⁶ because the closeness of vibrational energy levels in SiF_4 and GeH_4 favors near-resonant energy transfer. Rough estimations indicate that $\text{V} \rightarrow \text{V}$ transfer should be completed within tens of nanoseconds,⁶⁶ and this estimate is in accord with data for other systems.^{23,26,67,68} Thus, it may be assumed that equilibration of vibrational energy is achieved during the laser pulse.

It is known that collisional V-R,T energy-transfer processes proceed at rates that are a few orders of magnitude slower.⁶⁶ In the absence of pertinent data for the actual systems examined, we used available rate constants for V-R,T energy exchange, characteristic of some systems containing SiF_4 ,⁶⁷ GeH_4 ,⁶⁹ and SiH_4 ,^{70,71} in order to obtain some estimate of the time scale for these processes. This admittedly rough estimation clearly demonstrates that, under our experimental conditions, the time for the completion of V-R,T energy equilibration is of the order of tens of microseconds. Similar conclusions have been drawn for other systems.^{23,26,68} All the above considerations demonstrate that total thermalization of the absorbed energy may be achieved in times as long as are expected for the completion of chemical processes.^{19-21,72}

Mechanism of Photosensitized Decomposition. Energy absorption by the sensitizer and subsequent energy-transfer processes produce highly vibrationally (or thermally) excited germane molecules (GeH_4^*) which may undergo decomposition. The final products of dissociation are, as mentioned above, metallic Ge and H_2 . It is, however, not very likely that two molecules of H_2 are detached from the germanium central atom simultaneously. Most probably it occurs in two stages involving slow primary step(s). Essentially two primary pathways can be considered, viz.



The probabilities for both decomposition channels are primarily determined by the energetics of the reactions. Since excitation, under our experimental conditions, shows features of thermal excitation, one may expect that the channel with the lower energy barrier is more probable. According to available thermochemical data,^{43,44} the endothermicities of these two reactions are 165 and 364 kJ/mol, respectively. Examination of available kinetic information indicates that both processes have activation barriers^{43,44,62} in addition to the endothermicities. RRKM estimations⁶¹ indicate that, for such a large energy difference between these reaction channels, any participation of (7) will be negligible. There is also some experimental evidence to confirm the above conclusions. To detect decomposition according to (7), we performed irradiations in the presence of ethylene, which is known as an efficient radical trapping agent especially for H atoms.^{73,74} If H atoms or other kinds of radicals were involved in the decom-

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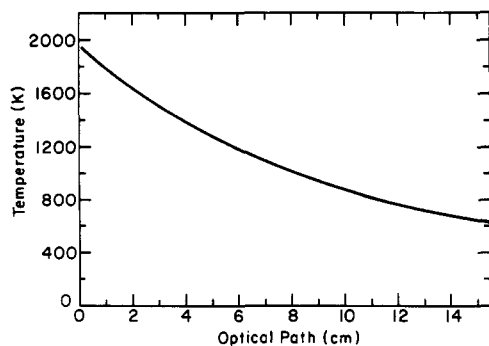


Figure 7. Distribution of temperature created originally in an absorption volume versus optical path upon irradiation of [GeH₄]:[SiF₄] = 1:1 mixture at a total pressure of 12 Torr. $E_0 = 2.6$ J/pulse.

position, the added trapping agent should have some kind of observable effect on reaction yields; moreover, the formation of addition products would be expected. No such effects or products, however, were detected.

Decomposition of GeH₄ in the ground state should lead to the fragments in their ground electronic states, i.e., GeH₂(¹A₁) and H₂(¹Σ_g⁺).^{75,76} In order to test for the presence of germylene as an intermediate, we performed irradiations in the presence of 1,3-butadiene which is widely used as a diradical trapping agent, e.g., a silylene trapping agent.^{73,74,77} No evidence was found for the formation of appropriate addition product. On the other hand, in irradiations of SiH₄-SiF₄ mixtures in the presence of 1,3-butadiene, we were able to detect the appropriate addition product by mass spectrometry. Moreover, the existence of SiH₂ upon infrared decomposition of silane has been proved directly.⁷⁸ Two explanations account for the failure to detect GeH₂. Firstly, it has been reported that GeH₂ does not add efficiently to dienes,⁷⁹ and secondly, in our system, germylene may participate in fast secondary reactions.

Despite the fact that we were not able to confirm the presence of GeH₂ as an intermediate, the existence of the rate-determining step (6) seems to reasonably explain the observed dependencies and remains in accord with kinetic considerations to be presented subsequently. It is also worthwhile mentioning that GeH₂ has been detected upon UV photodissociation of germane^{32,34} and has been postulated as an intermediate in the thermal decomposition of the compound.^{43,44}

A comparison of the infrared photodecomposition and thermal decomposition of SiH₄^{25,26-29,80} and GeH₄^{2,35-44} reveals a major difference. The solid products from the decomposition of silane always contain considerable amounts of hydrogen, whereas decomposition of germane always leads to the formation of pure germanium. This difference, most probably, results from different reactivities of the pertinent divalent species. Thus, it seems that GeH₂ is not stable and easily decomposes to give Ge and H₂. As has been shown by Vosintsev et al.,⁴⁴ GeH₂ should decompose simultaneously during its formation by the primary decomposition of germane.

Kinetic Model for the Process. To obtain as complete a picture as possible regarding the SiF₄-sensitized decomposition of germane by pulsed CO₂ laser radiation, we considered three effects influencing chemical changes in the system, and thus the reaction yields.

Absorption of energy from the laser photon field causes excitation of molecules present in the irradiated volume. The amount

of energy absorbed can be evaluated from the equation

$$E_{\text{abs}} = E_0[1 - \exp(-OD)] \quad (8)$$

where OD is the optical density defined by (5). The excitation of molecules leads to an increase in the temperature. Considerations from the previous section indicate that *total* thermal equilibration does not, however, take place during the pulse. Nevertheless, to make the problem tractable, we assume that the energy absorbed is distributed thermally among the accessible degrees of freedom of molecules present in the absorption volume, instantaneously after the pulse. Assuming, further, ideal behavior of all gaseous components, we can determine the gas temperature from an expression relating the amount of energy absorbed and capacity of the system for storage of energy,¹⁹ namely

$$E_{\text{abs}} = \sum_i x_i \left\{ \frac{3}{2} R(T - T_0) + \frac{s_i}{2} R(T - T_0) + \frac{N_0 h c \sum_j g_j \bar{\nu}_j}{\exp[N_0 h c \bar{\nu}_j / (RT)] - 1} - \frac{1}{\exp[N_0 h c \bar{\nu}_j / (RT_0)] - 1} \right\} \quad (9)$$

In (9), c represents the speed of the light; x_i denotes the number of moles of component i in the absorption volume; i and j identify a component in the gas mixture and the vibrational transition in a given component, respectively; s_i represents the number of rotational degrees of freedom in the molecule; g_j is the degeneracy of a vibrational mode characterized by a wavenumber $\bar{\nu}_j$; and T and T_0 represent maximum temperature after absorption and ambient temperature, respectively. The meaning of other symbols has been given earlier.

Decomposition of GeH₄ to Ge and 2H₂ is exothermic by 93.0 kJ/mol (ΔH_4).⁸¹⁻⁸³ Thus, initial decomposition of the compound caused by energy absorption from the CO₂ laser photon field releases additional amounts of energy. The resulting increase in temperature can be evaluated from (9) upon substituting E_{abs} by $n(\text{GeH}_4)\Delta H_4$, where $n(\text{GeH}_4)$ expresses the amount of GeH₄ decomposed, and taking T and T_0 to represent maximum temperature after decomposition and maximum temperature after absorption, respectively. Of course, values of x_i in (9) must be adjusted to the actual composition of the gas mixture. This effect can contribute to the overall decomposition of GeH₄ if the compound is still present in a given reaction volume.

The last important effect in the sensitized decomposition initiated by infrared laser radiation is the formation of mechanical waves as a result of absorption and decomposition processes.¹⁹⁻²¹ Once rapid thermalization inside the reaction volume occurs, the temperature of the irradiated zone becomes much higher relative to that of surrounding cold gas. Since the heated gas is now at a higher pressure, it expands outward through the cold gas. The expansion wave causes the hot molecules to move into the surrounding volume and undergo rarefaction between cold molecules. This process causes a cooling of the reactant mixture and consequently quenches chemical reactions. If the wave expansion is adiabatic, then the rate for the process is determined by the velocity of sound (c_s), which is given by (10),⁸⁴ viz.

$$c_s = (\gamma RT / \bar{M})^{1/2} \quad (10)$$

where γ denotes the ratio of the actual heat capacity at constant pressure (c_p) to the heat capacity of the system at constant volume (c_v) and \bar{M} represents the mean molar mass of the mixture. Values of γ at a given temperature can be evaluated by statistical

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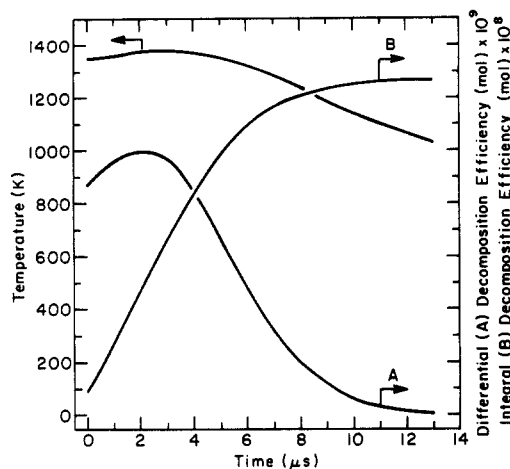


Figure 8. Evolution of temperature and both differential and integral dissociation efficiencies in time. Initial temperature in the layer = 1350 K; reactant mixture $[\text{GeH}_4]:[\text{SiF}_4] = 1:1$; total pressure = 12 Torr.

thermodynamics.⁸⁵ Generally, the expansion of a gas after heating by a laser pulse is not isoentropic in the entire time interval for the process. However, it can be assumed that expansion proceeds adiabatically for short periods of time. Other processes that could cause heat exchange between hot and cold gas would be convection and heat conduction; however, both of these latter effects contribute very little to the cooling of a gas mixture in the time expected for the completion of the pertinent chemical reactions.

Taking into account the three above-discussed effects, the yields of germane decomposition were evaluated by the procedure presented in detail in the Appendix. The solid lines in Figures 3–6 correspond to the theoretical reaction yields so calculated. Possibly to shed more light on the dynamics of the process, an example of the temperature distribution created in the irradiated volume as a result of the absorption process is shown in Figure 7. As expected, the temperature decreases on moving through the absorption volume. The temperature threshold for the decomposition depends on the partial pressures of reactants, and this arises from the RRKM behavior. Numerous calculations revealed, however, that observable dissociation occurs somewhere between 800 and 1000 K. Further insight into reaction dynamics is afforded by an analysis of the time evolution of dissociation efficiencies and temperature. The former magnitudes can be defined as differential or integral quantities. Differential dissociation efficiency expresses the number of moles of GeH_4 decomposed per unit time, whereas integral decomposition efficiency refers to the number of moles of GeH_4 decomposed over the entire time interval for the process. Figure 8 shows how the efficiencies of GeH_4 decomposition and the temperature change in a layer of gas having an initial temperature (created by the absorption process) of 1350 K. On the other hand, Figure 9 presents the lengthwise section of the absorption and reaction volumes in which the chemical changes in the system are completed, after the pulse, together with the appropriate decomposition profiles. The examination of the temperature evolution reveals that generally it decreases in time due to the expansion and rarefaction effects. If the temperature drops below a certain threshold value (800–1000 K), the decomposition of GeH_4 is quenched naturally. However, in some cases the process is stopped because the outer edge of the expanded hot gas reaches the cold walls of the cell. The time for the completion of chemical reaction extends from several microseconds to even 25 μs . This time is longer when the speed of the expansion wave is relatively low, and this takes place at fairly low temperatures.

The solid lines in Figures 3–6 do not exactly fit the experimental reaction yields. Nevertheless, given the complexity of the system, we think the general agreement is quite good. The source of the observed discrepancies might be that thermal equilibrium is not

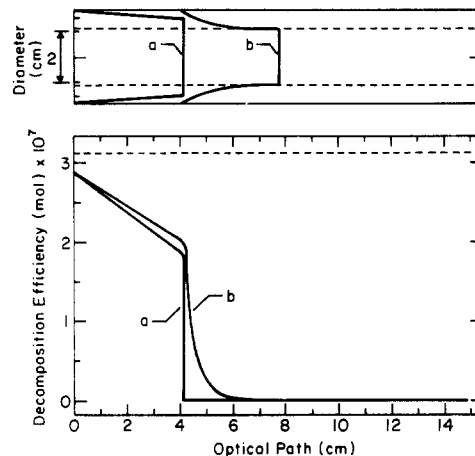


Figure 9. Lengthwise section of the absorption volume (indicated by dashed lines) and reaction volume (marked by solid lines), upper graph, together with the integral decomposition efficiency, lower graph, as a function of the geometry of an irradiation cell upon photolysis of $[\text{GeH}_4]:[\text{SiF}_4] = 1:1$ mixture at a total pressure of 12 Torr. $E_0 = 2.6$ J/pulse. Dashed line in the lower graph indicates the initial amount of GeH_4 in the cell. (a) denotes profiles corresponding to the extent of decomposition higher than 0.1 toward the amount of GeH_4 actually present in the layer in a given unit of time (0.1 level of accuracy). (b) indicates analogous profiles at the level of 0.001 (see Appendix).

in fact always reached. This will be particularly pronounced if the initial temperature created as a result of the absorption process is expected to be relatively high. Under those conditions, only equilibration of vibrational energy may be completed during the process.

Obviously, total thermal equilibrium (or even steady state) can never be attained in the system. Nevertheless, the thermal equilibrium hypothesis assumed in the model is quite well borne out, under our experimental conditions, as demonstrated by the results of the calculations. Moreover, the effect of foreign gases on the decomposition process clearly indicates that thermalization of the system must be far advanced. If equilibration of only vibrational energy were to take place during the process, one would not expect to observe an influence of helium on the decomposition yield. Both foreign gases quench the decomposition process as a result of the increase in the heat capacity of the system. The effect for H_2 is, however, more pronounced because of the possibility of accumulation of the energy into the vibrational degree of freedom of the molecule.

The model proposed in this work describes quite well the main features of the SiF_4 -sensitized decomposition of GeH_4 initiated by a pulsed CO_2 laser. It allows evaluation of the yields of GeH_4 decomposition exclusively on the basis of a knowledge of the molecular characteristics of the components in the reactant mixture and on parameters characterizing the absorption of energy by the system. While the model outlined in this work should not be accepted without any reservation, it forms a useful framework in which to consider the chemistry of photosensitized processes in the infrared region.

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Appendix

Since three effects, namely, absorption of energy, energetics of reaction, and shock-wave propagation, influence the decomposition process continuously, a description of their contributions requires the knowledge of appropriate analytical relationships. Due to the complex forms of (5) and (8)–(10), derivation of tractable analytical expressions relating $Y(-\text{GeH}_4)$ to parameters affecting the process is not feasible. Therefore, we solved the problem iteratively. For this purpose molecules belonging to the absorption volume were primarily singled out; this volume rep-

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resents an imaginary cylinder outlined by the beam cross section (3.5 cm², corresponding to the beam diameter equal to ca. 2.1 cm) and the optical path length of the cell. The absorption volume was then divided, transverse to the beam axis, into cylindrical layers having a base equal to the beam cross section and a thickness of 0.1 cm. When the system is irradiated, SiF₄ molecules absorb energy and E_{abs} values for each layer can be evaluated from (5) and (8). Assuming an instantaneous thermal equilibration in each layer, the maximum temperature was evaluated from (9) within the framework of the standard secant procedure (see e.g. Figures 7 and 8). In the latter estimation the following frequencies (in cm⁻¹) were used:⁹ for SiF₄, 800 (1), 268 (2), 1032 (3), and 389 (3); for H₂, 4397 (1). (The degeneracies of vibrations are indicated parenthetically.) To describe the behavior of the system in time, the chemical changes and shock-wave expansion were considered in 0.5- μ s units. At sufficiently high temperature decomposition of GeH₄ occurs. Thus, if the initial temperature (resulting from the absorption in the layer) is known, the amount of GeH₄ decomposed in the first unit of time can be derived from the standard unimolecular rate equation using k_{uni} values calculated by the RRKM method. (For details see Experimental Section.) Subsequently, the temperature after decomposition in the layer was evaluated on the basis of a relationship analogous to (9), as described earlier. Because the temperature changes only slightly from layer to layer, it can be assumed that expansion takes place only radially from the layer. Considering this effect in the first unit of time the increase of the diameter of a layer was evaluated on the basis of (10). Expansion and rarefaction of the gas brings about an increase in the number of molecules in our imagined extended layer. Thus, the temperature of a layer must decrease. If, again, an assumption of thermal equilibration is made, the temperature of the gas after expansion can be calculated on the basis of energy balances and the right-hand side of (9). This

temperature is the initial one for the determination of the amount of GeH₄ decomposed in the second time unit. Subsequently, the expansion effect was included for the second unit of time as described above. The iterations with respect to time were carried out until the amount of GeH₄ decomposed was less than 0.001 of that actually present in the layer (0.001 level of accuracy; Figure 8). Similar calculations were performed for the remaining layers. If the energy absorbed in the layer is relatively low, the resulting increase of temperature is not high enough to initiate chemical changes. Therefore, the iterations over the layers were stopped when decomposition of GeH₄ in the first time unit was less than 0.001 of that initially present in the layer. The yield of GeH₄ decomposition under given experimental conditions is the sum of contributions from the iterations carried out over all layers and units of time (Figure 9).

To evaluate the dissociation yields, a computer program was developed that took into account all the above-mentioned details and the calculations were performed on an IBM (Model PC XT/AT) personal computer.

To attempt to simplify the problem, we also carried out calculations assuming the same model for the process but using values of rate constants evaluated from the Arrhenius equation. The values of the Arrhenius activation energy and preexponential factor for these calculations were evaluated from the temperature dependence of $k_{\text{uni}}(T, \infty)$ values determined by the RRKM procedure.⁶¹ Unfortunately, decomposition yields thus derived did not fit well to the experimental ones. Similarly, if the time for the completion of reaction is chosen arbitrarily to be 10 μ s, as suggested by some authors,¹⁹⁻²¹ we do not obtain a satisfactory approximation of the experimental results.

Registry No. SiF₄, 7783-61-1; GeH₄, 7782-65-2; Ge, 7440-56-4; H₂, 1333-74-0.

Gas-Phase Reactions of AlO with Small Molecules[†]

J. Mark Parnis,[‡] S. A. Mitchell,* Tanya S. Kanigan, and Peter A. Hackett

Laser Chemistry Group, Division of Chemistry, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A 0R6 (Received: September 27, 1988; In Final Form: June 14, 1989)

AlO is produced in the gas phase at 296 K by reaction of Al atoms with N₂O following Al atom formation by multiphoton dissociation of trimethylaluminum (TMA). Production and decay of Al and AlO are monitored by laser-induced fluorescence. The combination of efficient vibrational relaxation of AlO by N₂O and low reactivity of AlO with N₂O at room temperature allows studies of AlO reaction kinetics to be carried out with a range of molecules using N₂O as a buffer gas. Second-order rate constants at 296 K (cm³ molecule⁻¹ s⁻¹) are reported for the reactions of ground-state Al(3²P_J) with N₂O, (1.1 ± 0.1) × 10⁻¹¹; ethylene oxide, (1.3 ± 0.1) × 10⁻¹⁰; and TMA, (1.3 ± 0.3) × 10⁻¹⁰ in Ar buffer gas, and for reactions of ground-state AlO(X²Σ⁺, v=0) with ethylene oxide, (2.1 ± 0.5) × 10⁻¹⁰; tetramethylethylene, (1.1 ± 0.4) × 10⁻¹¹; and TMA, (3.0 ± 1.0) × 10⁻¹⁰ in N₂O buffer gas. A third-order rate constant of (4.3 ± 0.4) × 10⁻³² cm⁶ molecule⁻² s⁻¹ is reported for the AlO + CO association reaction in N₂O buffer gas. Reactions of AlO with CO₂ and C₂H₄ showed buffer gas pressure dependent pseudo-second-order rate constants, indicative of processes involving formation of association complexes. Estimates are made of the upper limits for the rate constants for reaction of AlO with N₂O, methane, molecular hydrogen, isobutane, benzene, toluene, CF₃Cl, CF₃Br, and CCl₄, for which the reaction rates at 296 K were negligible.

Introduction

Recently, we have undertaken studies of the reactions of gas-phase Al and Ga atoms with small molecules.¹⁻⁴ We have found the formation of association complexes between these metal atoms and electron-pair donor molecules to be a general aspect of their chemical behavior near room temperature. Such association complexes are of interest in connection with model studies of active sites for adsorption of small molecules on metal surfaces and on

oxide-supported, metal-based catalysts.

In order to pursue this correlation, we have begun to examine other atomic and diatomic models for active sites in catalytic reactions. We report here an investigation of the reactions of a

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[†] Issued as NRCC No. 29469.

[‡] Present address: Department of Chemistry, Trent University, Peterborough, Ontario, Canada K9J 7B8.