

## THE DYNAMICS OF THE $\text{SiF}_4$ - SENSITIZED PROCESSES INITIATED BY A PULSED $\text{CO}_2$ LASER

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**Abstract** - A model enabling the examination of the dynamics of the  $\text{SiF}_4$  - sensitized processes initiated by a pulsed  $\text{CO}_2$  laser is outlined, taking into account three effects: energy absorption, energeticity of chemical reactions and expansion of hot gas created upon interaction of molecules with the infrared photon field. This approach was used to elucidate some aspects regarding the decomposition of  $\text{PH}_3$  and  $\text{GeH}_4$ .

### INTRODUCTION

Numerous molecules show absorption in the  $900\text{--}1100\text{ cm}^{-1}$  region and can thus be driven, by the  $\text{CO}_2$  laser, to the energy level necessary for the initiation of chemical processes. To reach such a level the absorption cross section and density of laser radiation have to be high enough. Unfortunately, this is not always achieved. Moreover, some compounds do not exhibit transitions in the emission region of the  $\text{CO}_2$  laser and their infrared photochemistry can not be studied directly. Photosensitization is a method used to carry out a photochemical process when a molecule can not be raised to the desired state by direct absorption of energy. The application of sensitizers, however, may result in the mechanism of the process differing from that characteristic for direct excitation. Photosensitized processes in the infrared region show many features of thermal processes in the fact that in both cases only thermal degrees of freedom are involved and energy is provided to the reacting molecule on collision.

In this paper a model is discussed which assumes that absorption of energy and subsequent energy transfer processes cause thermal excitation of molecules which decompose unimolecularly. This approach was adopted to get an insight into some aspects regarding infrared photochemistry of  $\text{PH}_3$  and  $\text{GeH}_4$ .

### EXPERIMENTAL

Experimental details have been given in our previous papers [1-3]. Briefly, the source of infrared radiation was a pulsed  $\text{CO}_2$  TEA laser (Lumonics, Model 103-2) tuned to either P40 or P42 line of the  $00^0_1 - 02^0_0$  transition. Irradiation was carried out with an unfocused beam whose central portion was separated by an iris. The irradiation's stainless steel cell had an optical length of 15.5 cm and a volume  $150\text{ cm}^3$ . Both ends of the cell were equipped with sodium chloride windows while transverse to the cylinder axis was a pinhole leak leading to the ionization region of a Bendix Model 14-101 time-of-flight mass spectrometer. It was assumed that ion current for the decomposing molecule was directly proportional to its partial pressure. The amounts of incident pulse energy ( $I_0$ ) and energy deposited in the system were measured by a Gen-Tec Model ED-500 Joulemeter.

### RESULTS AND DISCUSSION

#### *Energy Deposition*

In the systems considered in this work  $\text{SiF}_4$  is the only species interacting with the  $\text{CO}_2$  laser photon field. However, as was earlier reported [2-4], inert molecules may enhance the energy absorption. Moreover, the optical density of the systems absorbing  $\text{CO}_2$  laser radiation usually exhibits saturation type dependence on fluence and non-linear dependence on the optical path length and pressure of absorbing molecules [2-5]. This implies that the Beer-Lambert law is not obeyed under prevailing high radiation density conditions. Any considerations concerning the dynamics of  $\text{CO}_2$ -laser induced processes require knowledge of the amount of energy deposited in certain sites

of the reacting system. For such purpose the equation, shown below as (1), is convenient, being a modified form of the Beer-Lambert law, viz.

$$OD = \epsilon_0 \frac{1 + [C_0 + C_1(P_1/P_0)^{m_1} + \sum_i C_i(P_i/P_0)^{m_i}](I_0/I_c)}{1 + I_0/I_c} l \cdot P_1 \quad (1)$$

where OD is the optical density;  $P_1$ ,  $P_i$  and  $P_0$  are, respectively, the pressure of the absorbing gas ( $\text{SiF}_4$ ), pressure of the  $i$ -th non-absorbing component of the mixture, and the standard pressure (i.e. atmospheric pressure);  $l$  is the optical path length;  $I_0$  is the incident pulse energy; and  $\epsilon_0$ ,  $C_0$ ,  $C_1$ ,  $C_i$ ,  $m_1$ ,  $m_i$ , and  $I_c$  are empirical constants. Values of constants can be derived fitting (1) to the experimental data points. For  $\text{PH}_3$ - $\text{SiF}_4$  and  $\text{GeH}_4$ - $\text{SiF}_4$  systems they have been reported earlier [2,3].

Energy absorption and vibrational redistribution in the sensitizer occur in a time of the order of  $10^{-12}$  sec which is very short compared with the duration of the laser pulse ( $10^{-7}$  sec). The excited  $\text{SiF}_4$  molecules will tend to transfer energy to the molecules of their environment. Rough estimates performed using available data [6-10], suggest that  $V \rightarrow V$  transfer in numerous systems should be completed within tens of nanoseconds. The  $V \rightarrow R, T$  energy transfer processes are thought to be slower by even a few orders of magnitude. In our experimental conditions the energy equilibration time is of the order of microseconds. This is a time scale expected for the completion of chemical reactions involved.

#### Chemistry of Sensitized Decomposition of $\text{PH}_3$ and $\text{GeH}_4$

The problem has been discussed in details earlier [1-3].  $\text{SiF}_4$ -sensitized decomposition of  $\text{GeH}_4$  occurs in two stages:



and



However, only reaction (2) is the rate determining step. The overall process is exothermic since  $\text{GeH}_2$  species decomposes instantaneously during its formation.

Sensitized decomposition of  $\text{PH}_3$  is much more complex. Experimental data tend to indicate that the primary step involves the formation of molecular hydrogen and triplet phosphinidene radicals in reaction (4)



The latter species presumably participate in secondary processes whose nature is not known. To make the problem tractable we assumed that reaction (4) completes chemical changes upon  $\text{SiF}_4$ -sensitized decomposition of  $\text{PH}_3$ . This process is highly endothermic and requires the overcoming of a substantial activation barrier.

#### Dynamics of Photosensitized Processes

Dynamics of photosensitized processes is determined by overall chemical and physical changes following interaction of the system with the  $\text{CO}_2$  laser photon field. To examine this problem three effects are considered [2,3,11-13]: energy absorption, energeticity of chemical processes and shock wave expansion. The absorption of energy by a sensitizer and energy transfer processes cause heating of a gas mixture initially present in the absorption volume and subsequent decomposition of substrate molecules. The primarily formed species may participate in secondary processes that also affect the overall chemical changes in the system. Since the chemical reactions are accompanied by certain energetical effects they bring about a decrease (in the case of endothermic effect) or an increase (when exothermic effect) of the temperature and thus quench or enhance the primary decomposition, respectively. The absorption of energy creates a shock wave causing expansion of a hot molecules into the cool surrounding volume. The latter process causes cooling of the hot gas and quenches the primary decomposition considerably.

All the above-mentioned effects are included in the model which enables the evaluation of several characteristics of the reacting system. The model assumes that the absorbed energy is distributed randomly among the accessible thermal ( $V$ ,  $R$ ,  $T$ ) degrees of freedom of molecules present in the absorption volume and that this occurs instantaneously at the end of the pulse. Assuming,

further, ideal behaviour of all gaseous components, the microscopic temperature can be determined from an expression relating the amount of energy absorbed and capacity of the system for storage of energy, namely that shown in (5)

$$I_{\text{aba}} = \sum_i x_i \left\{ \frac{3}{2} R (T - T_0) + \frac{s_i}{2} R (T - T_0) + N_0 h c \sum_j g_j \nu_j \left[ \frac{1}{\exp [N_0 h c \nu_j / (RT)] - 1} - \frac{1}{\exp [N_0 h c \nu_j / (RT_0)] - 1} \right] \right\} \quad (5)$$

On the other hand, the amount of energy absorbed ( $I_{\text{abs}}$ ) can be evaluated from (6), i.e.

$$I_{\text{aba}} = I_0 [1 - \exp(-OD)] \quad (6)$$

In (5)  $R$ ,  $N_0$ ,  $h$  and  $c$  denote the gas constant, Avogadro number, Plank constant, and the speed of light, respectively;  $x_i$  represents the amount of a component  $i$  in the mixture;  $i$  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 wave number  $\nu_j$ ; and  $T$  and  $T_0$  represent the equilibrium temperature after absorption and ambient temperature, respectively.

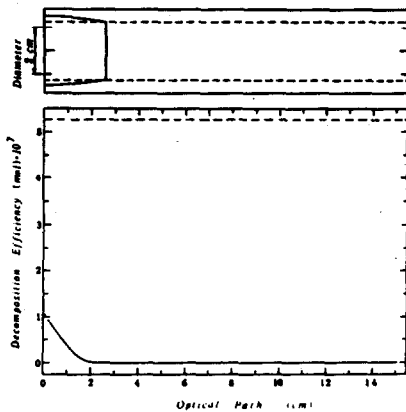


Figure 1

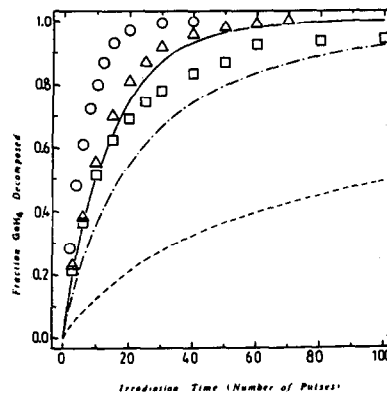


Figure 2

Fig.1. Lengthwise section of the absorption volume (indicated by dashed lines) and reaction volume (marked by solid lines), upper graph, together with decomposition efficiency, lower graph, as a function of the geometry of an irradiation cell upon photolysis of  $[PH_3] : [SiF_4] = 1:1$  mixture at the total pressure of 20 Torr.  $I_0 = 3.55$  J per pulse. Dashed line in the lower graph indicates the initial amount of  $PH_3$  in the cell.

Fig.2. Fraction of  $GeH_4$  decomposed versus irradiation time (number of pulses) at incident pulse energy = 1.8 J. Points represent experimental data and lines calculated from the model values: (O, —), for  $[GeH_4] : [SiF_4] = 1:3$  mixture (total pressure = 12 Torr); (□, - - -), for  $[GeH_4] : [SiF_4] = 3:1$  mixture (total pressure = 36 Torr); (△, - · - ·), for  $[GeH_4] : [SiF_4] : [He] = 1:1:2$  mixture (total pressure = 36 Torr).

The energetical effects resulting from chemical processes also influence the temperature of the system and can be described by an equation analogous to (5). In a simple case when decomposition of substrate is well defined, the changes in temperature resulting from the energeticity of the process can be evaluated substituting for the left hand side the quantity  $-n(\text{sub}) \times \Delta H(\text{sub})$ , where  $n(\text{sub})$  expresses the amount of substrate decomposed, and  $T$  and  $T_0$  represent the equilibrium temperature after decomposition and equilibrium temperature after absorption, respectively. Values of  $x_i$  in (5) must, of course, be adjusted to the actual composition of the gas mixture.

The energy absorption and rapid thermalization inside the reaction volume cause the temperature of the irradiated zone to be much higher than that of the surrounding cold gas. Due to the differences in pressure, and thus density, the hot gas expands outwards through the cold gas. The expansion wave causes the hot molecules to move into the surrounding volume and undergo rarefaction between cold molecules. Assuming isentropic expansion the rate of the process is determined by the velocity of sound ( $c_s$ ), viz.

$$c_s = \left( \frac{\gamma RT}{M} \right)^{1/2} \quad (7)$$

In (7),  $\gamma$  is the ratio of the heat capacity at constant pressure ( $c_p$ ) to the heat capacity at constant volume ( $c_v$ ) and  $M$  represents the mean molar mass of the mixture. Assuming complete thermal equilibration at any stage of expansion, the temperature can be evaluated on the basis of energy balances and right hand side of (5).

To evaluate temperature profiles, i.e.  $T$  versus time and geometry of the reaction zone, the standard second procedure can be applied.

Since the three above-mentioned effects influence the decomposition process continuously, it is not feasible to derive an analytical expression which would relate temperature and decomposition yield continuously. The problem can be solved, however, iteratively. For this purpose the whole process was considered dividing the absorption volume on imaginary thin layers. The initial layer is outlined by the beam cross section and thickness of the layer (e.g. 0.1 cm). This layer is allowed to expand in time. In our experimental conditions it is radial expansion which mainly contributes to the overall process. To describe the behaviour of the system in time, the chemical changes and shock wave expansion are considered in chosen time units (e.g. 0.5  $\mu$ sec). Following this approach and assuming that substrate decomposes unimolecularly the yield of reaction ( $R(\text{sub})$ ) can be derived from equation (8), viz.

$$R(\text{sub}) = \sum_i \sum_l n_{i,l} [1 - \exp(-k\tau_i)] \quad (8)$$

where  $n_{i,l}$  represents the initial amount of substrate in the layer before each iteration<sup>1</sup> (established on the basis of the actual composition of a gas mixture);  $i$  and  $l$  indicate summation over units of time and layers, respectively;  $k$  is the unimolecular rate constant calculated by RRKM method; and  $\tau$  represents unit of time.

Similar procedures can be used for the examination of other features of photosensitized processes.

Examples of the application of the model are given in Figs. 1 and 2. Fig. 1 represents the lengthwise section of the absorption volume upon irradiation of  $\text{PH}_3 - \text{SiF}_4$  system and reaction volume in which the chemical changes are completed, after pulse, together with the appropriate decomposition profile. On the other hand, Fig. 2 compares experimental and calculated decomposition yields upon exposure of  $\text{GeH}_4 - \text{SiF}_4 - (\text{He})$  systems by many pulses.

Concluding, the model presented enables the evaluation of the reaction yields, as well as other characteristics such as: extent of reaction in function of time and geometry of reaction zone, temperature profiles, etc., exclusively on the basis of a knowledge of the molecular characteristics of the compounds in the reactant mixture and on parameters characterizing the absorption of energy by the system.

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