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THE IR MULTIPHOTON DECOMPOSITION OF PH_3–SiH_4 MIXTURES SENSITIZED BY SiF_4

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Summary

The SiF_4-photosensitized decomposition of PH_3–SiH_4 mixtures by IR radiation at 1025.3 cm^{-1} results in the formation of H_2, SiH_3PH_2 and Si_2H_6 in the gas phase and a solid deposit which is probably a mixture of polymeric P–Si hydrides ($PSiH_x$). The effects of the composition of the reactant mixture, the pressure, the incident pulse energy and the presence of foreign gases (helium and nitrogen) on the course of the reaction were investigated. It was found that SiH_3PH_2 and Si_2H_6 are formed solely by the insertion of SiH_2 into PH_3 and SiH_4 respectively. A mechanism involving excitation of SiF_4 by absorption of radiation from the CO_2 laser beam and further collisional energy transfer between SiF_4^* and other molecules present in the system is in accord with the experimental results.

1. Introduction

IR multiphoton dissociation of small molecules occurs predominantly by the lowest energy channel and usually only a small excess of energy is contained in dissociation fragments. These facts differentiate IR multiphoton decomposition from UV dissociation, the latter often leading to highly excited fragments and/or fragments with excess kinetic energy. From this point of view, IR photochemistry may provide very useful methods of production of certain radical species and hence may be of importance in the study of reaction mechanisms, chemical kinetics and chemical synthesis.

As part of a general research program concerned with the study of silicon hydride and phosphorus hydride free-radical chemistry, we have extended our photochemical investigations to the IR region. In other publications the IR multiphoton decompositions of SiH_4 [1] and PH_3–SiH_4 mixtures [2], as well as the decomposition of SiH_4 [3] and PH_3 [4] sensi-

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tized by SiF_4 have been reported. In the present work we report on the SiF_4-photosensitized decomposition of the PH_3–SiH_4 system.

This problem was called to our attention for two reasons.

(a) The lowest energy decomposition channels for PH_3 [5] and SiH_4 [1, 6, 7] can be expressed by

$$PH_3 + nh\nu \longrightarrow PH(\tilde{X}\,^3\Sigma^-) + H_2(\tilde{X}\,^1\Sigma_g^+) \tag{1}$$

$$SiH_4 + nh\nu \longrightarrow SiH_2(\tilde{X}\,^1A_1) + H_2(\tilde{X}\,^1\Sigma_g^+) \tag{2}$$

By analogy with well-established reactions of diradical species [8, 9] quite different reactivity of the decomposition fragments $PH(\tilde{X}^3\Sigma^-)$ and $SiH_2(\tilde{X}^1A_1)$ toward other reactants present in the system is expected. Thus the study of SiF_4-photosensitized reactions in the PH_3–SiH_4 system presents the opportunity of examining the competitive behavior of these species. This particular system was chosen for study because the IR [2] and UV photochemistries [10] have already been investigated.

(b) Formation of solid products in the SiF_4-photosensitized multiphoton decomposition of the PH_3–SiH_4 system may occur in a manner similar to that found in the IR multiphoton decomposition of analogous systems [1 - 4, 11]. Amorphous silicon hydride films are widely applied as absorption layers in photocells and solar cells [12 - 14], and, although hydridic phosphorus films have not been used for these purposes as yet, investigations of the properties of hydridic silicon films doped with phosphorus have been carried out [15 - 19]. The results of this study may be useful in the development of new methods of production of hydrogenated amorphous Si–P films of technological importance.

2. Experimental section

The irradiations were carried out in a cylindrical stainless steel cell of 152 cm^3 volume (optical length, 15.5 cm) fitted with NaCl windows and coupled via a pinhole leak to a time-of-flight mass spectrometer. The source of IR radiation was a pulsed CO_2 transversely excited atmospheric pressure laser operated at 0.5 Hz and at a gas flow ratio of $He:CO_2:N_2 = 6.0:2.0:0.7$. All irradiations were carried out using an unfocused beam and with the laser tuned to the P42 line (1025.3 cm^{-1}) of the 00^01–02^00 transition of SiF_4. The whole beam was used with an effective irradiation area of 6 cm^2. The ratio of the irradiated volume to the total volume of the irradiation cell was about 0.6. Other experimental details concerning the apparatus, the experimental conditions and the measurements of the beam energy have been presented elsewhere [4].

Si_2H_6 was made by the reduction of Si_2Cl_6 (Petrarch) with $LiAlH_4$ (Alfa Products) using a method described earlier [20].

PH_2SiH_3 was prepared using the method of Sabherwal and Burg [21] and purified as described earlier [10].

Helium (purity, 99.995%), nitrogen (purity, 99.99%), hydrogen (purity, 99.95%), PH_3 (purity, 99.999%), SiF_4 (purity, 99.6%), C_2H_4 (purity, 99.98%),

C_2H_6 (purity, 99.96%) and n-C_4H_{10} (purity, 99.98%), all obtained from Matheson, and SiH_4 (electronic grade) obtained from Linde were used as received. All gas mixtures were prepared using a Saunders–Taylor apparatus [22].

Reaction products were identified by comparison of the overall mass spectrum resulting from the irradiation with the individual spectra of H_2, Si_2H_6 [23, 24] and PH_2SiH_3 [25]. The changes in concentrations of the substrates PH_3 and SiH_4 and of the products H_2, SiH_3PH_2 and Si_2H_6 during the photolyses were monitored by measurements of the intensities of the ion currents at m/z values of 34 a.m.u., 30 a.m.u., 2 a.m.u., 64 a.m.u. and 58 a.m.u. respectively. The intensity at $m/z = 2$ a.m.u. was corrected for the small contributions from PH_3 and SiH_4. Because of the relatively small yields of SiH_3PH_2 and Si_2H_6, no corrections to the ion currents of the substrates and H_2 due to either of these products were made. The calibration constant β_2 for H_2, which relates the current at $m/z = 2$ a.m.u. to the concentration of H_2, was determined by using the pure substance diluted with rare gases to the concentration ranges encountered in the photolyses. In the case of Si_2H_6 and SiH_3PH_2 it was not convenient to measure the calibration constants β_{58} (Si_2H_6) and β_{64} (PH_2SiH_3) in the same direct manner because of the thermal instability of these compounds. A satisfactory technique was to establish the calibration constants for Si_2H_6 and PH_2SiH_3 relative to β_{34} from PH_3 [26].

The reaction yields, in terms of moles per pulse, were determined from the changes in the appropriate ion currents. To attain good accuracy it was necessary to choose the number of pulses for irradiation which caused depletion of at least 10% of each substrate; the number of pulses required was between 1 and 50. With a maximum of 50 pulses it was not possible, at the highest partial pressures of substrates used, to measure decomposition yields of substrates because the fraction decomposed was so small. Each experimental value of the reaction yield was taken as a mean from at least five replicate measurements.

3. Results

3.1. General nature of the reactions

The IR multiphoton decomposition of PH_3–SiH_4 mixtures sensitized by SiF_4 results in the formation of H_2, as the major gaseous product, and a solid deposit coating the walls of the irradiation cell. Small amounts of phosphorus- and silicon-containing gaseous hydrides which have mass peaks with m/z values from 56 to 64 a.m.u. were also identified. The residual spectrum after subtraction of relative ion abundances for Si_2H_6 (based on the intensities of the unambiguous ions with m/z values of 56, 57 and 58 a.m.u.) was in good agreement with that of a synthetic sample of SiH_3PH_2. Moreover, the parent ion mass spectrum of the photolysis product recorded in this m/z region with an ionizing energy of 11 eV indicated the presence of only two ions, namely one at m/z = 62 a.m.u. ($Si_2H_6^+$) and the other at m/z = 64 a.m.u. ($SiH_3PH_2^+$). Examination of the overall mass spectrum of the gaseous products gave no indication of the formation of P_2, P_4 or higher homonuclear or mixed hydrides. The formation of these higher mass hydrides of silicon and SiP might have been expected on the basis of previous investigations [1, 2].

The ion currents *versus* time (or equivalently the ion currents *versus* the number of pulses) are presented in Fig. 1. It can be seen from these curves that all products are formed simultaneously with the decomposition of the substrates. The concentrations of SiH_3PH_2 and Si_2H_6 reach maximum values after about 20 pulses and then start to decrease, reaching almost zero by the end of the photolysis. However, the ratio $[SiH_3PH_2]/[Si_2H_6]$ was found to be constant during the course of irradiation with a value of about 3.2. The ratio $[PH_3]_{\mathrm{depleted}}:[SiH_4]_{\mathrm{depleted}}:[H_2]_{\mathrm{formed}}$ is equal to 1:1.5:3.4 at the beginning of photolysis; it reaches a value of 1:1.55:3.8 after about 20 pulses and drops to 1:1.25:3.2 at the end of the irradiation. This means that an increase in the number of pulses results in more of the hydrogen (produced from the decomposition of both substrates) remaining in the gas phase. The rates of all processes (in terms of moles per pulse) decrease with an increase in the irradiation time or, equivalently, in the number of pulses.

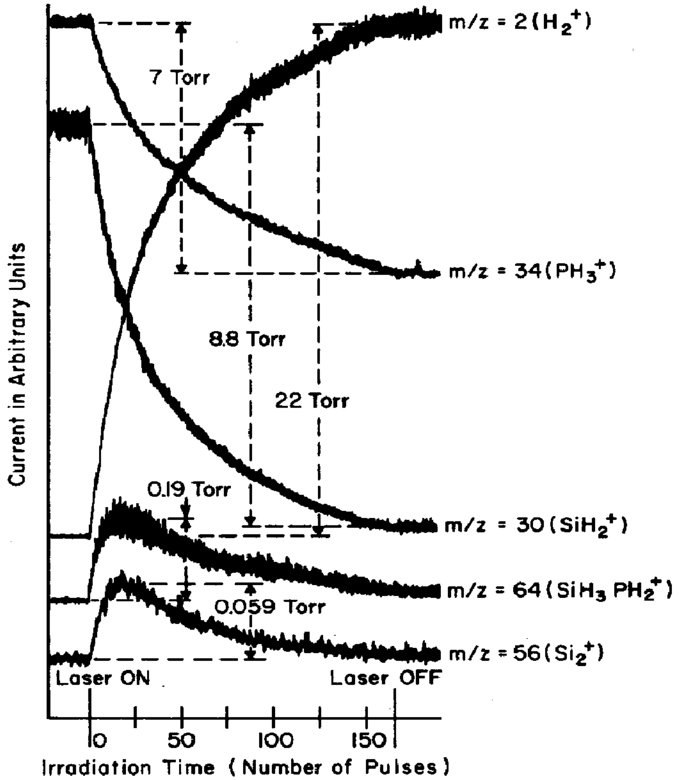

Fig. 1. Photolysis of a $[PH_3]$:$[SiH_4]$:$[SiF_4]$ = 2:2:1 mixture at a total pressure of 25 Torr and an incident pulse energy of 3.70 J.

3.2. *Reaction yields*

The extent of the reaction is reported in terms of the reaction yields $Y(i)$ defined by

$$Y(\pm i) = \frac{\text{number of moles of substance decomposed (or formed) per pulse}}{\text{energy absorbed per pulse}} \qquad (3)$$

Only SiF_4 absorbs the laser radiation, and, if we make the approximation that this absorption does not depend on the presence of other substances in the reactant mixture, the amounts E_{abs} of energy absorbed at various partial pressures p_{SiF_4} of SiF_4 can be calculated from [4]

$$E_{abs} = E_0[1 - \exp\{-(0.065 p_{SiF_4}{}^{0.63} + 0.048) p_{SiF_4}\}] \qquad (4)$$

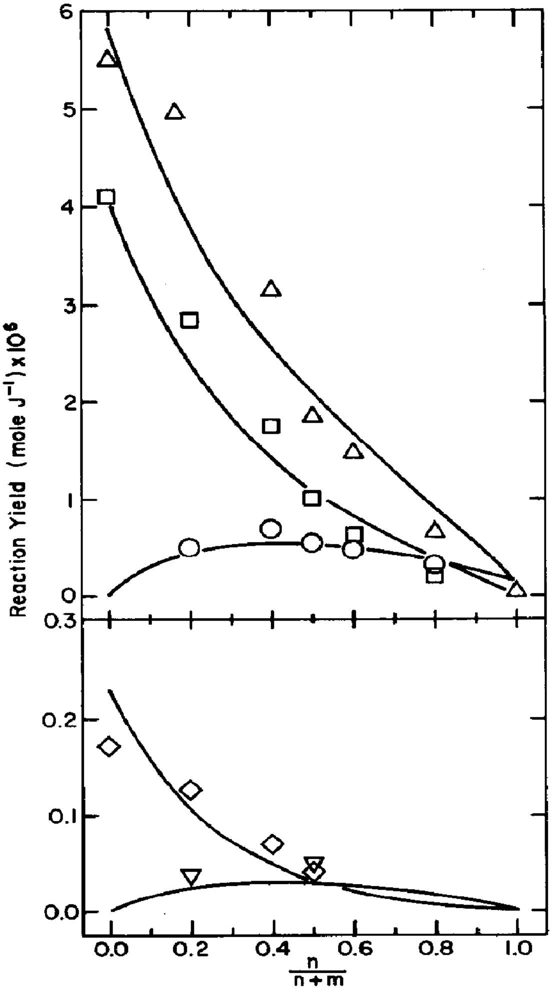

Fig. 2. Reaction yields as a function of the composition of the reactant mixture at incident pulse energy of 3.70 J (p_{PH_3}:p_{SiH_4}:p_{SiF_4} = n:m:5 (Torr) where $n + m$ = 20 Torr): ○, $Y(-PH_3)$; □, $Y(-SiH_4)$; △, $Y(H_2)$; ▽, $Y(PH_2SiH_3)$; ◇, $Y(Si_2H_6)$.

where E_0 represents the incident pulse energy (the amount of energy transmitted by the empty cell) expressed in joules.

The dependences of the reaction yields on the composition of the reactant mixture, the pressure, the incident pulse energy and the presence of foreign gases are presented in Figs. 2 - 7.

The reaction yields depend strongly on the composition of the reactant mixture, as shown in Fig. 2. Figures 3 and 5 indicate the threshold nature of the decomposition. At a constant composition of the reactant mixture ($[PH_3]:[SiH_4]:[SiF_4]$ = 2:2:1) the decomposition is achieved at pressures p_{SiF_4} as low as 2 Torr. With an increase in the partial pressure of SiF_4 the reaction yields increase, reaching a maximum at p_{SiF_4} = 7 Torr, and then start to decrease slightly. At a partial pressure of SiF_4 of 5 Torr and a constant ratio $[PH_3]/[SiH_4]$ of unity, the reaction yields decrease with an increase in the partial pressures of PH_3 or SiH_4 (Fig. 4). Figure 5 shows the strong dependence of the reaction yields on the incident pulse energy. This is behavior typical of many substances in an intense IR laser field [27 - 30]. The reaction yields decrease strongly in the presence of helium and nitrogen as shown in Figs. 6 and 7 respectively. Similar dependence on foreign gases has been found in the IR multiphoton decomposition of other substances [27, 29].

3.3. Photolyses in the presence of ethylene

As was mentioned earlier the IR multiphoton-induced dissociation of PH_3 and SiH_4 is expected to take place by the lowest energy channels available, which for this system are represented by reactions (1) and (2). The next higher decomposition channels for the two compounds would be dissociation to $H(^2S)$ atoms and to the $PH_2(\tilde{X}\,^2B_1)$ [5] and SiH_3 [6, 31] radicals respectively. If the latter decompositions did actually occur, some hydrogen

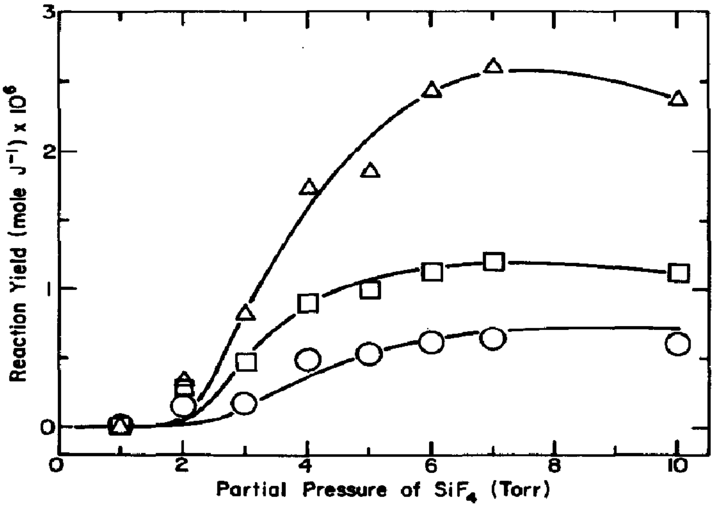

Fig. 3. Reaction yields as a function of the total pressure at an incident pulse energy of 3.70 J ($p_{PH_3}:p_{SiH_4}:p_{SiF_4}$ = 2:2:1 (Torr)): ○, $Y(-PH_3)$; □, $Y(-SiH_4)$; △, $Y(H_2)$.

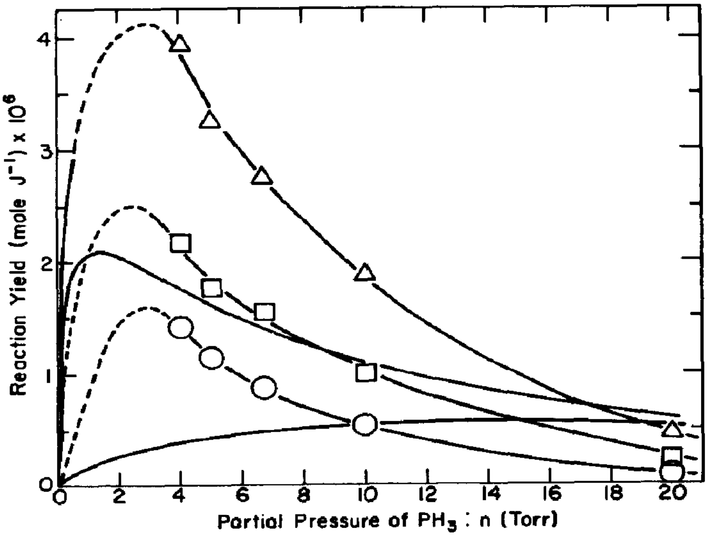

Fig. 4. Reaction yields as a function of the partial pressure of PH_3 (or SiH_4) at an incident pulse energy of 3.70 J ($p_{PH_3}:p_{SiH_4}:p_{SiF_4} = n:n:5$ (Torr)): ○, $Y(-PH_3)$; □, $Y(-SiH_4)$; △, $Y(H_2)$.

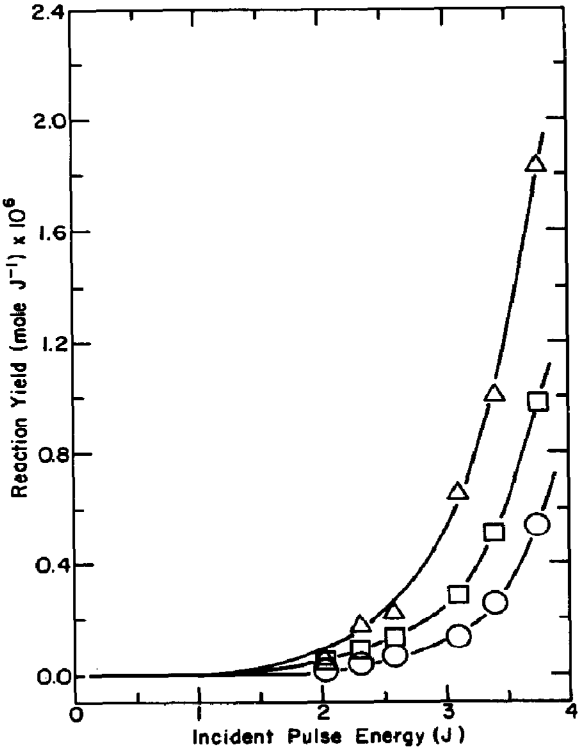

Fig. 5. Dependence of the reaction yields on the incident pulse energy at $p_{PH_3}:p_{SiH_4}:p_{SiF_4} = 10:10:5$ (Torr): ○, $Y(-PH_3)$; □, $Y(-SiH_4)$; △, $Y(H_2)$.

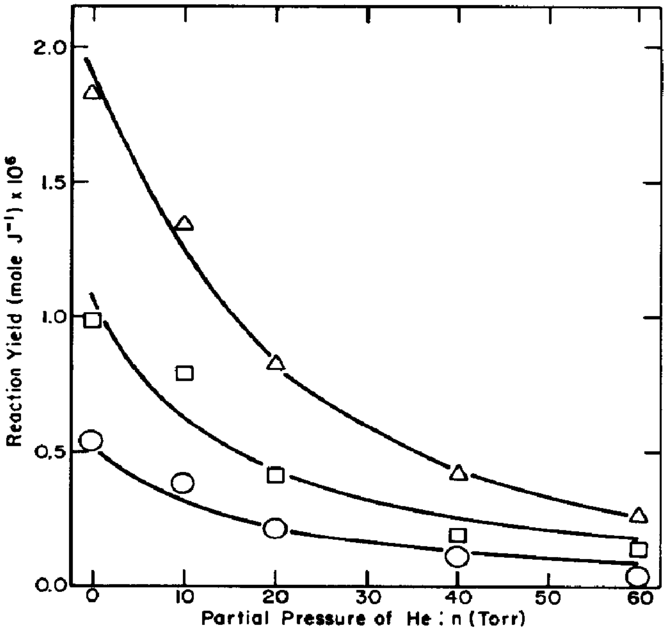

Fig. 6. Reaction yields in the presence of helium at an incident pulse energy of 3.70 J (p_{PH_3}:p_{SiH_4}:p_{SiF_4}:p_{He} = 10:10:5:*n* (Torr)): ○, $Y(-PH_3)$; □, $Y(-SiH_4)$; △, $Y(H_2)$.

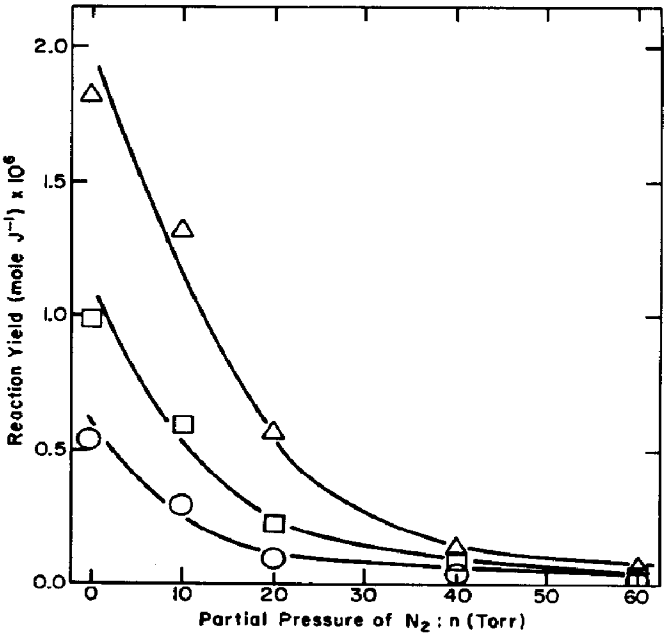

Fig. 7. Reaction yields in the presence of nitrogen at an incident pulse energy of 3.70 J (p_{PH_3}:p_{SiH_4}:p_{SiF_4}:p_{N_2} = 10:10:5:*n* (Torr)): ○, $Y(-PH_3)$; □, $Y(-SiH_4)$; △, $Y(H_2)$.

atom addition to ethylene would be expected to take place in the presence of ethylene and would be followed by the formation of ethane and *n*-butane [32]. Since neither ethane nor butane could be detected, these two higher energy decomposition channels can be excluded at our level of detection sensitivity.

The SiF_4-photosensitized IR multiphoton decomposition of a PH_3–SiH_4–C_2H_4 mixture results in the formation of gaseous products exhibiting mass peaks with m/z values from 52 to 64 a.m.u. and from 40 to 45 a.m.u. Our previous work [4] has shown that the only gaseous product of the SiF_4-photosensitized decomposition of PH_3–C_2H_4 mixtures is molecular hydrogen. It has also been found [4] that, under the same experimental conditions, the SiF_4–C_2H_4 system does not undergo any chemical changes during IR irradiation. Taking into account the above considerations, we are led to the conclusion that a new product is formed in the SiF_4 photosensitization of PH_3–SiH_4–C_2H_4 mixtures, most probably by reaction of $SiH_2(\tilde{X}\,^1A_1)$ with C_2H_4. This product has also been reported in the direct IR multiphoton decomposition of the PH_3–SiH_4–C_2H_4 system [2]. The fact that the same compound was formed in both systems was confirmed by direct IR multiphoton decomposition of an SiH_4–C_2H_4 mixture and by SiF_4-photosensitized IR decomposition of an SiH_4–C_2H_4 mixture. Both the residual mass spectrum (after subtraction of that for Si_2H_6) and the analogy with the major product of the reaction of $(CH_3)_2Si$ with C_2H_4 [33] suggest strongly that the compound is $CH_2{=}CH{-}SiH_3$ formed by the addition of $SiH_2(\tilde{X}\,^1A_1)$ across the double bond [34] and a subsequent rearrangement.

3.4. *Solid product*

The solid product can be seen directly as a brown deposit coating the walls of the irradiation cell. The solid film formed on the front window is not transparent to visible radiation but is transparent to the IR laser radiation, however, since its IR spectrum indicates no absorption bands above 1000 cm^{-1}. This suggests that the removal of the solid deposit from the windows of the irradiation cell after each irradiation is not necessary; however, we found that too long an irradiation through a window not subjected to cleaning caused cracking of the window material at the coated surface.

The IR spectrum of the solid deposit on the front window shows two broad bands. The first one, in the region from 2200 to 2300 cm^{-1}, was also seen in the solid film formed upon SiF_4-photosensitized dissociation of PH_3 [4] and can be ascribed to a P—H stretching mode. The second broad band appears at about 900 cm^{-1} and presumably arises from $=SiH_2$ bending vibrations [35]. The latter absorption was not observed in the deposit formed during the SiF_4-photosensitized decomposition of PH_3 [4]. The IR spectrum of the solid product in this work differs from that of the solid film resulting from the direct IR multiphoton decomposition of PH_3–SiH_4 mixtures [2]. In the latter case two additional bands around 2140 and 2200 cm^{-1}, which are probably due to Si—H stretching modes [35], were clearly observed.

The composition and the structure of the solid deposits have not been studied. The previously described test for the identification of phosphorus among solid products of photolysis [4, 26] gave no positive results and thus indicates that all phosphorus in the solid is bonded to other elements, *i.e.* phosphorus or P–Si hydrides. Material balances, made with the assumption that one-third of the hydrogen from PH_3 is found in the solid phase [4], suggest that about a quarter or less of the hydrogen from SiH_4 is found in the solid products.

4. Discussion

4.1. Nature of the primary processes

The IR absorption spectra indicate that neither PH_3 nor SiH_4 absorbs CO_2 laser radiation at 1025.3 cm^{-1} [4, 6], and hence irradiation of these compounds at this frequency, separately or in mixtures, does not cause any chemical changes. Decomposition of the above systems is observed, however, when irradiations are carried out in the presence of SiF_4 as a photosensitizer.

Some aspects of the use of SiF_4 as an IR photosensitizer, as well as several problems concerning the mechanism of the energy exchange, have been discussed in our previous work [4]. In such irradiations the SiF_4 absorbs energy from the IR laser field in a multiphoton process and the excited SiF_4 molecules produced may exchange energy by collision with other components of the system. In this way excited PH_3 or SiH_4 molecules appear. Some of these may have energies at or above the respective decomposition barriers and these molecules may decompose to smaller fragments. Therefore the absorption process can be described as follows:

$$SiF_4 + nh\nu \xrightarrow{n<b} SiF_4{}^* \qquad (5)$$

$$SiF_4 + nh\nu \xrightarrow{n>b} (SiF_4{}^*)_D \qquad (6)$$

$$SiF_4 + nh\nu \xrightarrow{n<a} SiF_4{}^{**} \qquad (7)$$

$$SiF_4 + nh\nu \xrightarrow{n>a} (SiF_4{}^{**})_D \qquad (8)$$

where a and b represent the energy barriers for decomposition which are expressed as the number of IR photons at 1025.3 cm^{-1} for PH_3 and SiH_4 respectively. X^{**} (or X^*) denotes a molecule which contains excess energy up to the lowest dissociation pathway of PH_3 (or SiH_4) and $(X^{**})_D$ (or $(X^*)_D$) indicates a molecule containing excess energy at least as great as the lowest decomposition pathway of PH_3 (or SiH_4).

4.2. Reaction mechanism

With one component to absorb energy and two components to receive this energy by collision and to decompose to molecular fragments, the mechanism is necessarily very complex. On the basis of the experimental facts and our previous considerations [4] the reaction mechanism must account for the following: (a) collisional deactivation of vibrationally excited SiF_4, SiH_4 and PH_3 by non-excited components of the system; (b) dissociation of PH_3 and SiH_4 molecules excited above the appropriate decomposition thresholds; (c) formation of SiH_3PH_2, Si_2H_6 and H_2; (d) formation of a solid deposit. The most satisfactory mechanism for the chemical change, as deduced from the experimental work reported here and in previous studies of the IR multiphoton decomposition of SiH_4 [1] and SiH_4–PH_3 mixtures [2] and of the SiF_4-photosensitized decomposition of SiH_4 [3] and PH_3 [4], is shown by eqns. (5) - (34):

$$(SiF_4^{**})_D + SiF_4 \longrightarrow 2SiF_4^* \tag{9}$$

$$(SiF_4^{**})_D + PH_3 \longrightarrow SiF_4^* + PH_3^* \tag{10}$$

$$(SiF_4^{**})_D + PH_3 \longrightarrow SiF_4^* + (PH_3^*)_D \tag{11}$$

$$(SiF_4^{**})_D + SiH_4 \longrightarrow SiF_4^* + SiH_4^* \tag{12}$$

$$(SiF_4^{**})_D + SiH_4 \longrightarrow SiF_4^* + (SiH_4^*)_D \tag{13}$$

$$(SiF_4^{**})_D + M \longrightarrow SiF_4^* + M^* \tag{14}$$

$$(SiF_4^*)_D + SiF_4 \longrightarrow 2SiF_4^* \tag{15}$$

$$(SiF_4^*)_D + PH_3 \longrightarrow SiF_4^* + PH_3^* \tag{16}$$

$$(SiF_4^*)_D + SiH_4 \longrightarrow SiF_4^* + SiH_4^* \tag{17}$$

$$(SiF_4^*)_D + SiH_4 \longrightarrow SiF_4^* + (SiH_4^*)_D \tag{18}$$

$$(SiF_4^*)_D + M \longrightarrow SiF_4^* + M^* \tag{19}$$

$$(PH_3^*)_D + SiF_4 \longrightarrow PH_3^* + SiF_4^* \tag{20}$$

$$(PH_3^*)_D + PH_3 \longrightarrow 2PH_3^* \tag{21}$$

$$(PH_3^*)_D + SiH_4 \longrightarrow PH_3^* + SiH_4^* \tag{22}$$

$$(PH_3^*)_D + M \longrightarrow PH_3^* + M^* \tag{23}$$

$$(PH_3^*)_D \longrightarrow PH(\tilde{X}\,^3\Sigma^-) + H_2(\tilde{X}\,^1\Sigma_g^+) \tag{24}$$

$$(SiH_4^*)_D + SiF_4 \longrightarrow SiH_4^* + SiF_4^* \tag{25}$$

$$(SiH_4^*)_D + PH_3 \longrightarrow SiH_4^* + PH_3^* \tag{26}$$

$$(SiH_4^*)_D + SiH_4 \longrightarrow 2SiH_4^* \tag{27}$$

$$(SiH_4^*)_D + M \longrightarrow SiH_4^* + M^* \tag{28}$$

$$(SiH_4^*)_D \longrightarrow SiH_2(\tilde{X}\,^1A_1) + H_2(X\,^1\Sigma_g^+) \tag{29}$$

$$SiH_2 + PH_3 \longrightarrow PH + SiH_4 \tag{30}$$

$$SiH_2 + PH_3 + B \longrightarrow SiH_3PH_2 + B \tag{31}$$

$$SiH_2 + SiH_4 + B \longrightarrow Si_2H_6 + B \tag{32}$$

$$PH \xrightarrow{(wall)} PH(s) \tag{33}$$

$$SiH_2 \xrightarrow{(wall)} SiH_n(s) + (1 - 0.5n)H_2 \tag{34}$$

On the basis of the available thermochemical and kinetic data [36 - 42] an energy corresponding to at least 20 photons at 1025.3 cm^{-1} must be acquired by an SiH_4 molecule to cause its decomposition according to reaction (29). However, energy corresponding to 32 or more photons at 1025.3 cm^{-1} must be accumulated in PH_3 to cause its dissociation according to reaction (24). Hence, in view of this photosensitized decomposition, SiF_4 molecules with excitation energies above 20 IR photons must be distinguished from those possessing energies above 32 photons. The former, which are denoted by $(SiF_4^*)_D$, contain enough energy for the decomposition of SiH_4 only, while the latter, which are denoted by $(SiF_4^{**})_D$, have sufficient energy to cause dissociation of either PH_3 or SiH_4.

Molecular hydrogen, as a stable product of the decomposition of both substrates, remains in the gas phase. However, two reactive products of the primary dissociation, namely $PH(\tilde{X}\,^3\Sigma^-)$ and $SiH_2(\tilde{X}\,^1A_1)$, undergo further reactions (reactions (30) - (34)). On the basis of our previous work [2, 4] the only reaction in which PH participates is formation of the solid deposit, as depicted by reaction (33). The SiH_2 molecules formed in reaction (29) are much more reactive than PH and undergo insertion reactions into SiH_3 and PH_3, as shown by reactions (30) - (32). This same pattern of reactivity has been observed previously in studies of the vacuum UV photodecomposition of SiH_4–PH_3 mixtures [9].

Most of the silicon contained in the reacted SiH_4 molecules must appear in the solid product since SiH_3PH_2 and Si_2H_6 are the only observed gaseous products and the yields are too low to account for all of the silicon reacted. Therefore reaction (34) is proposed to account for this fact.

4.3. *Kinetic treatment of the mechanism*

Extension of the kinetic treatment presented in our previous work [4] on SiF_4–PH_3-photosensitized decomposition to the mechanism depicted by reactions (5) - (34) leads to straightforward but very cumbersome expressions because a second and more reactive component, *i.e.* SiH_4, has been added to the system. These expressions describe the dependences of all reaction yields on several parameters such as the composition of the reactant mixtures (*i.e.* the partial pressures of all components), the incident pulse energy and the rate constants of the elementary reactions in the mechanism.

A few of the pertinent rate constants are known, and, if these are combined with reasonable initial guesses and iterations for those that are unknown, it can be shown that the kinetic expressions derived from the mechanism in reactions (5) - (34) are in semiquantitative agreement with the experimental data in Figs. 2 - 7.

Undoubtedly the complete mechanism of the SiF_4-photosensitized decomposition of PH_3–SiH_4 mixtures is even more complicated than that shown by reactions (5) - (34). Nevertheless, some qualitative conclusions can be drawn from the derived kinetic results. Our calculations confirm that the decomposition of PH_3, according to reaction (24), requires an energy corresponding to at least 11 photons at 1025.3 cm^{-1} above the endothermicity [5]. In contrast, the decomposition of SiH_4 according to reaction (29) takes place almost without an activation barrier in excess of the endothermicity, a fact that is in accord with previous observations [38 - 42]. This conclusion may also explain another experimental fact, namely that SiH_4 is decomposed by a non-focused laser beam at a fluence of about 1 J cm^{-2} while the decomposition of PH_3 cannot be achieved under the same conditions [1].

The energy exchange between $(SiF_4^*)_D$ and SiH_4 molecules appears to be much more efficient than the energy transfer between $(SiF_4^{**})_D$ and PH_3. This conclusion, together with the above discussion, explains the lower decomposition yields for PH_3 compared with those for SiH_4. The relative rates of quenching of all the excited molecules in the system by inert gases are higher for nitrogen than for helium. This is not an unexpected result, since nitrogen molecules have internal degrees of freedom available and helium does not.

The observed yields of formation of SiH_3PH_2 and Si_2H_6 are surprisingly low. At the pressures obtaining in our experiments it is unlikely that reaction (34) is faster than reactions (31) and (32) [38]. A more convincing explanation is that the photosensitized dissociation of both SiH_3PH_2 and Si_2H_6 is faster than that of SiH_4. To test this hypothesis we carried out irradiations of PH_3, SiH_4 and Si_2H_6 in the presence of SiF_4 as photosensitizer. For a substrate-to-SiF_4 ratio of 1:9 and a total pressure of 10 Torr, we found $Y(-PH_3):Y(-SiH_4):Y(-Si_2H_6) = 1:7:14$. Thus Si_2H_6 is decomposed by excited SiF_4 molecules much faster than are the simpler substrates PH_3 and SiH_4, and we assume that this is probably also true for SiH_3PH_2. This fact may also account for the absence of Si_3H_8 and higher silanes from the products. The latter substances have been observed in the direct IR multiphoton decomposition of SiH_4–PH_3 mixtures [2].

According to the kinetic calculations the factor n in reaction (34) is close to unity. This means that half the hydrogen from SiH_2 is transferred to the solid products. This is consistent with the fact that vibrational modes of $—SiH_2—$ and $—PH—$ were seen in the IR spectrum of the solid deposit. If it is assumed that all bonds are saturated, then the solid deposit is probably constructed from $(SiH_2)_x$, $(PH)_y$ or $(SiH_2—PH)_z$ units and amorphous silicon. It is worth mentioning that similar compositions of the solid products have been observed in the vacuum UV photodissociation of PH_3–SiH_4 mixtures [10].

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