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MONOSILYLPHOSPHINE FORMATION BY RAPID SILYLENE INSERTION IN THE IR PHOTOCHEMISTRY OF SiH_4–PH_3 MIXTURES†

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Summary

Monosilylphosphine is a major product of the IR multiphoton-induced decomposition of SiH_4–PH_3 mixtures carried out in such a way that only SiH_4 absorbs IR radiation from a pulsed CO_2 laser. The reaction forming monosilylphosphine is that of a very rapid insertion of silylene into a P—H bond of PH_3, a process occurring with a rate coefficient of 8.8×10^{-13} cm^3 molecule^{-1} s^{-1} at room temperature. Monosilylphosphine is not stable in the presence of large excesses of SiH_4 and PH_3 and decomposes to unidentified products at ambient temperature in a pseudo-first-order reaction.

1. Introduction

Monosilylphosphine was first observed by Fritz [1, 2] as a product of the thermal decomposition of SiH_4 at 450 °C in the presence of PH_3, the latter compound not itself undergoing a measurable thermal decomposition at temperatures below 550 °C. Although a mechanism was not proposed in this early work [1, 2], in a later review article Fritz [3] suggested the following reaction scheme:

$$SiH_4 \rightarrow SiH_3 + H \qquad (1)$$

$$H + PH_3 \rightarrow H_2 + PH_2 \qquad (2)$$

$$SiH_3 + PH_2 \rightarrow SiH_3PH_2 \qquad (3)$$

Nearly a decade after the discovery of monosilylphosphine, Jolly and coworkers [4 - 6] showed that when SiH_4–PH_3 mixtures are passed through an electric discharge monosilylphosphine is formed together with disilylphosphine, diphosphine and various polysilanes. Although a mechanism was

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not proposed, the action of the electric discharge certainly produces hydrogen atoms and silyl radicals together with other reactive transients and the results are therefore consistent with the suggestion that the formation of monosilylphosphine occurs via reactions (1) - (3).

More recently, it has been reported [7] from this laboratory that small amounts of monosilylphosphine are formed in the 147 nm photolysis of SiH_4–PH_3 mixtures carried out in such a way that over 90% of the radiation is absorbed by PH_3. While the principal transients formed in this photochemical study [7] were PH and PH_2 radicals, radical scavenging and isotopic labeling studies led to the conclusion that monosilylphosphine was formed exclusively by reaction (3), *i.e.* PH did not undergo an insertion reaction into the Si—H bonds of SiH_4.

Despite the fact that monosilylphosphine is formed by reaction (3) in the vacuum UV photodecomposition of SiH_4–PH_3 mixtures (and very probably also in the electric discharge decomposition [4 - 6]), the evidence is now conclusive [8 - 10] that the initiation step in the thermal decomposition of SiH_4 is the reaction

$$SiH_4 \rightarrow H_2 + SiH_2 \qquad (4)$$

and not reaction (1). Therefore it follows that reaction (3) is not the source of monosilylphosphine in the thermal decomposition experiments of Fritz [1, 2]; rather, this product is most likely due to the insertion of silylene, formed in reaction (4), into a P—H bond of PH_3. However, this insertion reaction has not to our knowledge been reported.

It has recently been shown in this laboratory [11] that reaction (4) is the almost exclusive decomposition path initiated when SiH_4 at room temperature and pressures above 10 Torr is irradiated with the P(20) line (944.19 cm^{-1}) of the 10.6 μm band of a pulsed CO_2 transversely excited atmospheric pressure (TEA) laser at a fluence per pulse of 1.0 J cm^{-2}. Since PH_3 does not absorb significantly at this IR frequency, irradiation of an SiH_4–PH_3 mixture should test the hypothesis that silylene will insert into P—H bonds and, if so, will perhaps permit measurement of the rate coefficient for the reaction.

2. Experimental details

The IR laser photodecomposition was carried out in a cylindrical stainless steel cell 3.45 cm in diameter and 15.5 cm long with a volume of 152 cm^3. A pinhole leak, located in the wall of the photolysis cell, led directly to the ionization source of a time-of-flight mass spectrometer. The ends of the photolysis cell were fitted with KCl windows sealed in place by O-ring supports, and the cell was mounted so that the laser beam was perpendicular to the axis of the time-of-flight mass spectrometer. After leaving the photolysis cell, gas molecules traversed a distance of 18.5 cm before encountering the electron beam of the ionization chamber. The pressure on

the ion source side of the pinhole was such as to ensure a mean free path between collisions of at least 500 cm. Thus molecules leaving the photolysis cell reached the ionization source with a transit time on the millisecond time scale.

The source of IR radiation was a CO_2 TEA laser (Lumonics Research Ltd., model 103-2) pulsed at a frequency of 0.5 Hz. All irradiations were carried out with an unfocused beam and with the laser tuned to the P(20) line of the 10.6 μm band at 944.19 cm^{-1}, corresponding to a photon energy of 0.117 06 eV. The incident energy per pulse, as measured with a GenTec joulemeter and an empty photolysis cell, was found to be 6.6 J which for the beam diameter of 2.95 cm corresponds to a fluence per pulse of 1.0 J cm^{-2}. The beam illuminated approximately 75% of the photolysis cell volume. All photolyses were carried out with equimolar SiH_4–PH_3 mixtures at a total pressure of 60 Torr. Under these conditions absorption of the laser beam is essentially complete [11] with the average number of photons absorbed per SiH_4 molecule (in the irradiated zone) per pulse being equal to 3.5.

The gaseous products of the IR laser photolysis were identified by mass spectra of the reacting mixture taken before, during and after the reaction. The dependences of the reactant and product concentrations on the reaction time (or equivalently on the number of laser pulses at 0.5 Hz) were determined by continuous monitoring of appropriate ion currents as follows: H_2 (H_2^+, m/q = 2 a.m.u.); SiH_4 (SiH_2^+, m/q = 30 a.m.u.); PH_3 (PH_3^+, m/q = 34 a.m.u.); Si_2H_6 (Si_2^+, m/q = 56 a.m.u.); SiH_3PH_2 ($SiH_3PH_2^+$, m/q = 64 a.m.u.); Si_3H_8 (Si_3H^+, m/q = 85 a.m.u.). Calibration of the mass spectrometer to enable conversion of the ion currents to partial pressures was based on the mass spectra of pure samples.

SiH_4 was obtained from the Matheson Company, purified by vacuum distillation and stored in a reservoir on the vacuum line. PH_3 (99.999% pure), also obtained from Matheson, was used as received. Si_2H_6 and Si_3H_8 were prepared by the methods described previously [12]. SiH_3PH_2 was prepared by the method of Sabherwal and Burg [13] as described in a previous report [7].

3. Results and discussion

3.1. Photolysis of the SiH_4–PH_3 mixture

The products of the IR laser photolysis are H_2, SiH_3PH_2, Si_2H_6, Si_3H_8, traces of higher silanes and a brown to reddish-brown solid containing phosphorus, silicon and hydrogen. The absence of any significant ion intensity at m/q = 65 a.m.u. and m/q = 66 a.m.u. indicates the absence of P_2H_4 [14 - 17]; however, small amounts of P_2 would have eluded detection. Although the spectra of Si_2H_6 [18] and SiH_3PH_2 [19] overlap in the 59 - 62 a.m.u. range, Si_2H_6 and SiH_3PH_2 are easily identified by the ion currents in the m/q ranges 56 - 58 a.m.u. and 63 - 64 a.m.u. respectively. Although there is considerable overlap of the mass spectra of $(SiH_3)_2PH$ and $Si_2H_5PH_2$ with

that of Si_3H_8, the presence of ion currents at m/q = 93 a.m.u. and m/q = 94 a.m.u. that are far in excess of isotopic contributions from $Si_3H_8^+$ (m/q = 92 a.m.u.) suggest that $(SiH_3)_2PH$ and/or $Si_2H_5PH_2$ are formed. The intensities of these ions were, however, too small for a reliable time dependence study.

The rate of the IR-laser-induced decomposition of SiH_4 and PH_3 is shown in Fig. 1 in which the partial pressures of the reactants are plotted *versus* the total irradiation time or equivalently the number of laser pulses. The time dependence of the product partial pressures is shown in Fig. 2, from which it is clearly seen that all are primary reaction products. The points shown in both these figures were taken from continuous recorder tracings of ion currents *versus* time. The absence of any indication of steps in these tracings indicates that the reactant depletion and product build-up are monotonically increasing functions of the number of laser pulses, thus confirming the fact that the mean residence time of a molecule in the photolysis cell (about 1000 s) is very long compared with the time between laser pulses (2 s). As will be discussed later, the actual chemical reactions induced by a laser pulse are very fast compared with the time between pulses.

It can be seen in Fig. 2 that Si_2H_6 and Si_3H_8 approach the steady state partial pressures typical of a flow system much more rapidly than do H_2 and SiH_3PH_2. This very rapid approach to the steady state has been observed

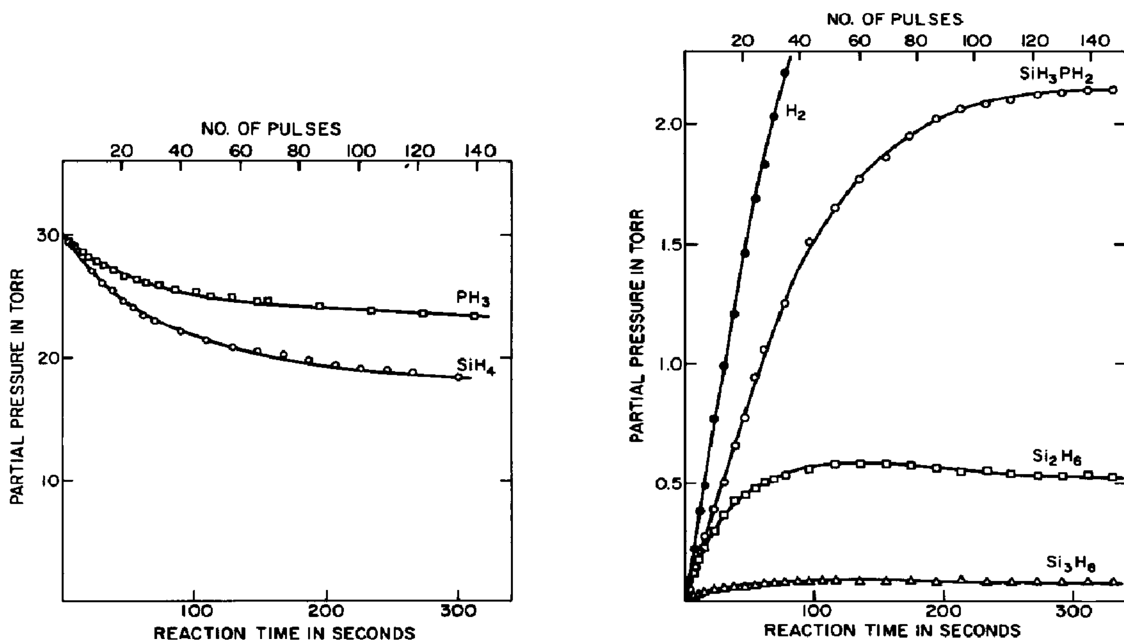


Fig. 1. Time dependence of the depletion of reactants induced by IR laser irradiation at 944.19 cm^{-1} and a fluence of 1.0 J cm^{-2}: ○, SiH_4; □, PH_3.

Fig. 2. Time dependence of product formation in the IR laser irradiation of SiH_4–PH_3 mixtures at 944.19 cm^{-1} and a fluence of 1.0 J cm^{-2}: ●, H_2; ○, SiH_3PH_2; □, Si_2H_6; △, Si_3H_8.

before in the hydrogen-atom-induced decomposition [20] and vacuum UV photodecomposition [21] of SiH_4 and has been attributed to the onset of a surface reaction of Si_2H_6 and Si_3H_8 with adsorbed silicon hydrides.

It has been shown previously [11] that the initiation step in the IR-laser-induced decomposition of SiH_4 is reaction (4), which occurs for SiH_4 molecules which have acquired 21 or more photons of 944.19 cm^{-1} radiation. We have strengthened this conclusion by examination of the IR-laser-induced decomposition of SiH_4 at 944.19 cm^{-1} in the presence of C_2H_4. The absence of any indication of C_4H_{10} and C_2H_6 formation means that H atoms and hence SiH_3 radicals are not formed [22]. Both these facts indicate that processes (1) - (3) do not occur to any significant extent in the IR laser photochemistry of SiH_4.

Since only SiH_4 absorbs the laser radiation and SiH_2 is the only reactive entity produced by this absorption, we can conclude that SiH_3PH_2 is formed by the insertion of SiH_2 into a P—H bond of PH_3, just as Si_2H_6 is formed by a similar insertion into an Si—H bond of SiH_4. Combining this conclusion with the mechanism proposed for the IR laser photodecomposition of pure SiH_4 [11], we have, subsequent to reaction (4), the scheme

$$SiH_2 + PH_3 \rightleftarrows SiH_3PH_2^* \quad (5)$$

$$SiH_2 + SiH_4 \rightleftarrows Si_2H_6^* \quad (6)$$

$$Si_2H_6^* \rightarrow SiH_3SiH + H_2 \quad (7)$$

$$SiH_3PH_2^* + M \rightarrow SiH_3PH_2 + M \quad (8)$$

$$Si_2H_6^* + M \rightarrow Si_2H_6 + M \quad (9)$$

$$SiH_3SiH + SiH_4 \rightarrow Si_3H_8^* \quad (10)$$

$$SiH_3SiH + PH_3 \rightarrow Si_2H_5PH_2^* \quad (11)$$

etc.

with Si_3H_8 and $Si_2H_5PH_2$ being formed by collisional deactivation of the products of reactions (10) and (11).

From the reported value of k_6 [23] we calculate that the mean lifetime of SiH_2 under our conditions is of the order of microseconds. Since the time between laser pulses is 2 s, the chemical reactions initiated by an individual laser pulse are therefore completed long before the onset of the next pulse. If we make the reasonable assumption that the fractions of $SiH_3PH_2^*$ and $Si_2H_6^*$ that are collisionally stabilized are equal, the ratio of the initial rate of formation of SiH_3PH_2 to that of Si_2H_6, determined from Fig. 2, is given by

$$\frac{(\mathrm{d}P(SiH_3PH_2)/\mathrm{d}t)_0}{(\mathrm{d}P(Si_2H_6)/\mathrm{d}t)_0} = \frac{k_5}{k_6} = 0.92 \pm 0.16 \quad (12)$$

In view of the fact that the absolute accuracy of the rate constant ratio depends on the validity of the assumption of equal stabilization probabilities for $SiH_3PH_2^*$ and $Si_2H_6^*$, the error limits given refer only to the precision of measurement of the ratio of initial rates.

At room temperature (300 K) the value of k_6 is 9.54×10^{-13} cm^3 molecule^{-1} s^{-1} [23] which combined with equation (12) yields, for the insertion of SiH_2 into PH_3,

$$k_5 = (8.8 \pm 1.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (13)$$

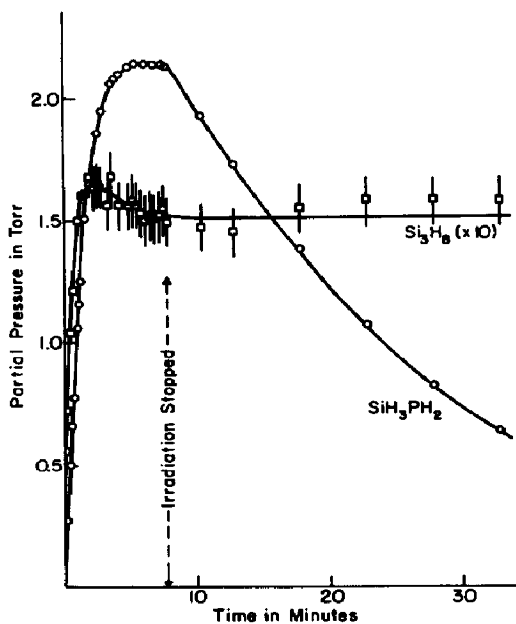
While the actual value of k_5 so derived is dependent on the assumption of equal probabilities of collisional stabilization, the assumption is sufficiently valid as to leave no doubt that the insertion of SiH_2 into P—H bonds is a very fast reaction.

The conclusion that SiH_2 inserts into the P—H bonds of PH_3 and the Si—H bonds of SiH_4 with comparable rates is in disagreement with the experimental observations of Sefcik and Ring [24], relative to the reactions of SiH_2 with CH_3PH_2 and CH_3SiH_3, although it is in accord with their *a priori* estimates of the relative rates. The actual value of k_5/k_6 reported here is about nine times higher than the indirect estimate made in our study of the vacuum UV photodecomposition of SiH_4–PH_3 mixtures [7]. While we are unable to account for this disagreement, we believe the value of the relative reactivity reported here to be more reliable since it was obtained by a much more direct measurement.

3.2. *Stability of SiH_3PH_2*

Examination of the mass spectra of the reacted mixture after the laser irradiation was stopped indicates that SiH_3PH_2 decomposes at the ambient temperature of the reaction cell. This can be seen in Fig. 3 in which the partial pressures of SiH_3PH_2 and Si_3H_8 are plotted *versus* time. The laser irradiation was started at time zero and continued until approximately steady state partial pressures of the two substances were reached. At 7.8 min the irradiation was stopped. It can be seen clearly from Fig. 3 that, while Si_3H_8 is stable over the time of the post-photolysis observation, a significant decomposition of SiH_3PH_2 occurs.

A semilogarithmic plot of the data is shown in Fig. 4, from which it can be seen that the decomposition reaction is first order in SiH_3PH_2 with a rate coefficient of 0.048 min^{-1}. This rapid decomposition of SiH_3PH_2 is unexpected in view of reports by Fritz [2, 3] that thermal decomposition becomes observable only at temperatures of 400 °C and above; moreover it has been shown [5] that $Si_2H_5PH_2$, which is expected to be less stable than SiH_3PH_2, undergoes only negligible decomposition in 1 day at room temperature. However, these reports [2, 3, 5] of the decomposition of SiH_3PH_2 and $Si_2H_5PH_2$ refer to the vapor of the pure compound, contained presumably in clean vessels, while in our experiments the SiH_3PH_2 is present in a large excess of SiH_4 (10:1) and PH_3 (11:1) and in a reaction vessel whose walls are coated with a solid film of silicon and phosphorous hydrides. It



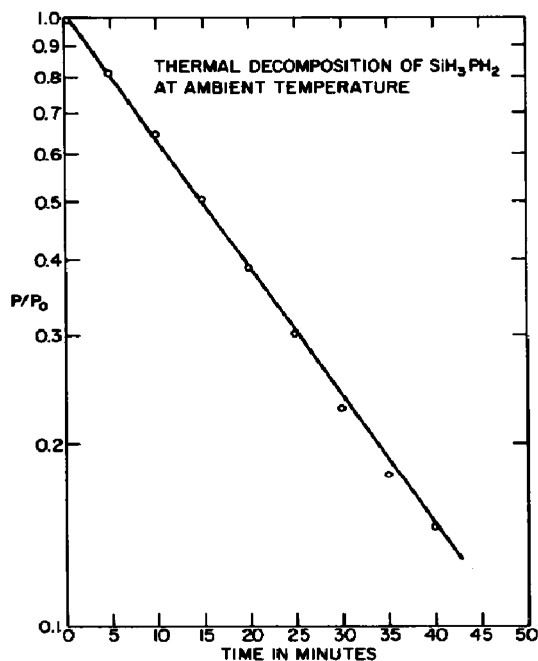


Fig. 3. Post-irradiation behavior of the products SiH_3PH_2 and Si_3H_8: ○, SiH_3PH_2; □, Si_3H_8.

Fig. 4. First-order plot of the partial pressure–time dependence of SiH_3PH_2 after termination of irradiation.

thus appears that SiH_3PH_2 is reacting at room temperature with the silicon and phosphorous hydride surfaces or with SiH_4 and/or PH_3 to form products as yet unidentified. Such a surface reaction could easily be first order in SiH_3PH_2 concentration, as demanded by the data in Fig. 4, and the reformation of PH_3 and SiH_4 or of surface-adsorbed products would have escaped detection in the present experiments. We believe that we would have detected Si_2H_6 (a likely product of a gas phase reaction between SiH_3PH_2 and SiH_4), and so we favor the surface reaction as an explanation for the decomposition.

Studies of this room temperature decomposition of SiH_3PH_2 are continuing.

3.3. Formation of solid

The brown to reddish-brown solid product observed is typical of the decomposition of silanes, phosphines and their mixtures. Comparison of the initial rates of formation of gaseous products (Fig. 2) with the initial rates of depletion of the reactants (Fig. 1) indicates that the recoveries of hydrogen, phosphorus and silicon in the gaseous products are 39%, 17% and 58% respectively. Assuming that the material unaccounted for is contained in the solid product, we estimate the solid composition to be 27 at.% H, 45 at.% P and 28 at.% Si; equivalently, this can be expressed by the approximate empirical formula $Si_3P_5H_3$.

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