# THE 147 nm PHOTOLYSIS OF PHOSPHINE–SILANE MIXTURES


J. BLAZEJOWSKI and F. W. LAMPE

*Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)*

## Summary

The 147 nm photochemistry of $PH_3$–$SiH_4$ mixtures was investigated at various ratios of the substrates such that more than 90% of the radiation was absorbed by $PH_3$. The photodecomposition of $PH_3$–$SiH_4$ mixtures results in the formation of $H_2$, $Si_2H_6$, $PH_2SiH_3$ and $P_2H_4$ in the gas phase and a solid deposit which is probably a mixture of phosphorus and polymeric phosphorus silicon hydrides $PSiH_x$. On photolyses of mixtures of the deuterated derivatives the analogous deuterated products are formed. The quantum yields for the gaseous products and for depletion of the substrates were measured. For the $PH_3$–$SiH_4$ system it was found that quantum yields depend on the composition of the reactant mixture and on the light intensity of the incident radiation. When deuterated compounds were used significant changes in all quantum yields were observed. Parent-ion mass spectrometric analysis of phosphorus- and silicon-containing volatile products indicates that $PH_2SiH_3$ is formed by two pathways: (i) combination of $PH_2$ and $SiH_3$ radicals; (ii) insertion of $SiH_2$ into $PH_3$. A mechanism involving primary photodissociation of $PH_3$ is proposed which is in accord with the experimental observations as well as with our knowledge of the photochemistry of pure $PH_3$ and $SiH_4$.


## 1. Introduction

As a part of a general research program concerned with the study of silicon and phosphorus hydride free-radical chemistry, we have extended our photochemical investigations to the $PH_3$–$SiH_4$ system. This problem was called to our attention for two reasons.

(1) As mentioned in our previous report [1], $P_2H_4$, formed in the 147 nm photolysis of $PH_3$, arises mainly by combination of $PH_2$ radicals; however, the gaseous products of the 147 nm photodecomposition of $SiH_4$ are formed mainly by insertion of appropriate silylene species into molecules of

the reactants [2]. The behaviour of PH$_3$ thus seems to be rather unusual because the vacuum UV photochemistry of many other compounds [3] indicates that formation of divalent species and their further reactions with reactants is usually the main route for formation of secondary products. The choice of the PH$_3$–SiH$_4$ system for investigation presents the opportunity to explore whether this anomaly arises from the general behavior of PH-type species or whether it is caused by some non-typical properties of PH$_3$ molecules. Moreover, under the conditions to be used, formation of SiH$_2$ is expected and hence the study presents the opportunity to examine the possible competition of substrates for the insertion reaction.

(2) Formation of a technologically important solid film may occur in a manner similar to that found in the vacuum UV photolysis of PH$_3$ [1] and SiH$_4$ [2]. Amorphous films of silicon hydride have been widely tested for use in photocells and solar cells [4, 5]. The analogous hydridic phosphorus films have not been examined for these purposes as yet, although investigations of the properties of hydridic silicon films doped with phosphorus have been conducted [6 - 9]. Phosphosilicate glass films have been used for other purposes [10, 11]. Knowledge of the photochemistry of PH$_3$–SiH$_4$ systems is therefore of considerable practical importance.

## 2. Experimental

The photolyses were carried out in a 38 cm$^3$ cylindrical stainless steel cell fitted with an LiF window and coupled via a pinhole leak (diameter, approximately 35 $\mu$m) to a time-of-flight mass spectrometer. This apparatus and the xenon resonance lamp used as a light source have been described previously [1].

The light intensity incident on the reactant mixture was determined by (CF$_3$)$_2$CO actinometry ($\Phi$(C$_2$F$_6$) from (CF$_3$)$_2$CO = 1.12 at 4 Torr) [12]. The photodecomposition of PH$_3$–SiH$_4$ mixtures produces a solid deposit on the walls and window of the photolysis cell which reduces the light intensity incident on the reactant mixture (Fig. 1). Because of this effect it was necessary to clean the window often, usually after a few experiments, as well as to make actinometric measurements prior to each photolysis.

P$_2$H$_4$ was prepared by the neutral hydrolysis of Ca$_3$P$_2$ (Alfa Products) in a previously described [1] modification of the method of Evers and Street [13]. PD$_3$ and P$_2$D$_4$ were prepared in the same manner except for the use of 99.8% D$_2$O, obtained from Alfa Products, in the hydrolysis.

Si$_2$H$_6$ was made by the reduction of Si$_2$Cl$_6$ (Petrarch) with LiAlH$_4$ (Alfa Products) using a method described earlier [14].

PH$_2$SiH$_3$ was prepared by the method of Sabherwal and Burg [15]. The crude product was evacuated for 1 h at 195 K and then for 2 h at 146 K (n-propanol slush bath). The residue was subjected to high vacuum fractional condensation in which the volatile material appearing during warm-up to 177 K (toluene slush bath) was condensed in a trap held at 195 K. When
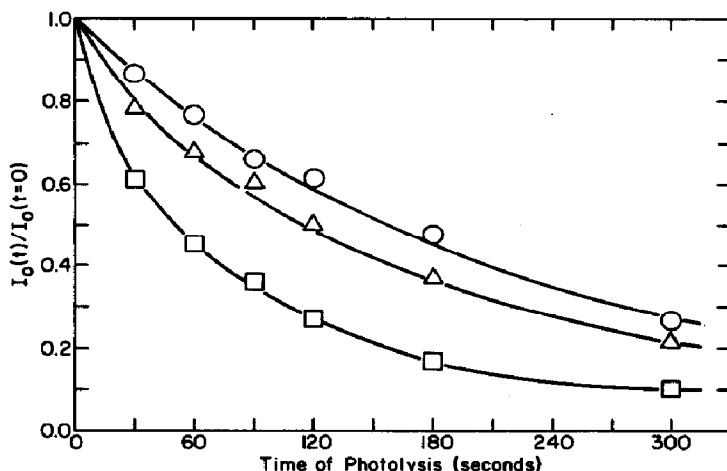
Fig. 1. Reduction in the incident light intensity by the formation of a film on the window of the photolysis cell after photolysis: □, $p(PH_3)$ = 0.48 Torr; ○, $p(PH_3)$ = 0.48 Torr + $p(SiH_4)$ = 0.225 Torr; △, $p(PH_3)$ = 0.48 Torr + $p(SiD_4)$ = 0.225 Torr. Gas mixtures in the photolysis cell were changed after every 30 s of irradiation.

mixtures with neon were prepared, $PH_2SiH_3$ was evaporated from a reservoir which was kept at 273 K. The mass spectrum of the compound obtained was similar to that published by Saalfeld and Svec [16] for $PH_2SiH_3$; however, somewhat different relative ion intensities were established. Some impurities were found in the compound prepared, the major impurity being $Si_2H_6$. It was possible to determine mass spectrometrically the amount of this compound present from the ion currents at $m/q$ values of 56, 57 and 58. Other impurities were in small amounts and were neglected.

Neon (99.995%), $H_2$ (99.95%) and $PH_3$ (99.999%), all from Matheson, and $D_2$ (99.5%, Linde), $SiH_4$ (electronic grade, Linde), $SiD_4$ (98 at.% D, Merck, Sharp and Dohme), $Si_2D_6$ (98 at.% D, Merck, Sharp and Dohme), $C_2F_6$ (PCR) and $(CF_3)_2CO$ (DuPont) were used as received.

From published vacuum UV absorption spectra, the absorption coefficients of $PH_3$ [17] and $SiH_4$ [18, 19] at 147 nm have been estimated to be $1.9 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ and $4 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ respectively. For deuterated derivatives the absorption coefficients were assumed to be the same. It was convenient to adjust the ratio of concentrations of both substrates such that one component absorbed by far most of the incident radiation. Thus, by keeping the ratio $\gamma = [PH_3]/[SiH_4] \geqslant 2$, $PH_3$ absorbed more than 90% of the total incident radiation in all experiments. Also, in all experiments the initial partial pressure of $PH_3$ was 0.48 Torr. Neon was used as a diluent gas in all experiments so that the total pressure in the photolysis cell was 40 ± 0.5 Torr. All gas mixtures were prepared using a Saunders–Taylor apparatus [20].

Reaction products were identified by comparison of the overall mass spectrum produced by the photolysis with the individual spectra of $H_2$, HD, $D_2$, $P_2H_4$ [21 - 23], $P_2D_4$ [21], $PH_2SiH_3$ [16], $Si_2H_6$ [24, 25] and $Si_2D_6$. The quantum yields for the loss of substrates and for formation of products

were determined by a method previously described [1]. There is no ion in the product mass spectra that is unique to $PH_2SiH_3$ and therefore corrections are necessary. The ion with $m/q = 60$ ($SiPH^+$ and $Si_2H_4^+$) was used to determine $PH_2SiH_3$. This ion arises from both $PH_2SiH_3$ and $Si_2H_6$ and has a relatively high intensity in both mass spectra. It was possible to calculate the part of $m/q = 60$ due to $Si_2H_6$ from the intensities of $m/q = 56$, $m/q = 57$ and $m/q = 58$ and the known mass spectrum of $Si_2H_6$.

Because of the complicated mixtures of phosphorus and silicon hydrides produced by the photolyses and the fairly low quantum yields of their formation, no corrections for contributions of products to the ion currents for $PH_3$ ($PD_3$) and $SiH_4$ ($SiD_4$) were made.

## 3. Results

### 3.1. General nature of the photodecomposition

The direct photolysis of $PH_3$–$SiH_4$ systems at 147 nm results in the formation of $H_2$ and a gaseous mixture of phosphorus- and silicon-containing hydrides which have mass peaks with $m/q$ values from 56 to 66. Mass spectra obtained after subtraction of relative ion abundances for $Si_2H_6$ (based on the intensities of the ions with $m/q$ values of 56, 57 and 58) and for $P_2H_4$ (based on the ion with $m/q = 66$) were in good agreement with that for the synthetic sample of $PH_2SiH_3$. Moreover, as shown in Table 1 the pure parent-ion mass spectrum of the photolysis product mixture recorded at 11 eV indicated the presence of only three ions at $m/q = 62$ ($Si_2H_6^+$), $m/q = 64$ ($PH_2SiH_3^+$) and $m/q = 66$ ($P_2H_4^+$). Examination of the overall mass spectrum gave no indication of the presence of $P_4$ or of higher phosphorus, P–Si or silicon hydrides in the gas phase other than those just described. It was difficult to check for the existence of $P_2$ in the gas phase. However, based on our previous results [1] the absence of $P_2$ molecules in the gas phase might be expected.

Similar results were obtained when appropriate deuterated substrates were used as may be seen in Table 1. Based on our knowledge of the vacuum UV photochemistry of $PH_3$ [1] and $SiH_4$ [2], PH (PD), $PH_2$ ($PD_2$), $SiH_2$ ($SiD_2$) and $SiH_3$ ($SiD_3$) intermediate species should be expected on irradiation of the reactant mixtures listed in Table 1. Thus, products of combination of monovalent radicals and of insertion of divalent radicals into molecules of substrates should appear in the photolyte. The mechanisms of formation of $P_2H_4$ [1] and $Si_2H_6$ [2] have been discussed previously and an analysis of the data in Table 1 suggests that $PH_2SiH_3$ is formed by two pathways: (i) combination of monovalent $PH_2$ and $SiH_3$ radicals; (ii) insertion of $SiH_2$ into $PH_3$. Examination of the parent-ion mass spectra in Table 1 gives no indication of formation of products by insertion of PH into $SiH_4$.

For $PH_3$–$SiH_4$ photolysis the ion current–time dependence curves for depletion of substrates and formation of products are presented in Figs. 2 and 3. The shapes of the curves indicate that all the products shown are

**TABLE 1**

Phosphorus- and silicon-containing gaseous products in the photolysis of $PH_3(PD_3)$-$SiH_4$-$(SiD_4)$ mixtures

| Reactants | Parameters from mass spectra in the region of phosphorus- and silicon-containing gas phase products | | |
|---|---|---|---|
| | Range of appearance of ions at 50 eV, m/q | m/q at 11 eV | Ions at 11 eV |
| $PH_3$-$SiH_4$ | 56 - 66 | 62 | $Si_2H_6^+$ |
| | | 64 | $PH_2SiH_3^+$ |
| | | 66 | $P_2H_4^+$ |
| $PH_3$-$SiD_4$ | 56 - 68 | 66 | $P_2H_4^+ + PH_2SiHD_2^+$ |
| | | 67 | $PH_2SiD_3^+$ |
| | | 68 | $Si_2D_6^+ + PHDSiD_3^+$ |
| $PD_3$-$SiH_4$ | 56 - 70 | 62 | $Si_2H_6^+$ |
| | | 66 | $PD_2SiH_3^+$ |
| | | 67 | $PD_2SiH_2D^+$ |
| | | 70 | $P_2D_4$ |
| $PD_3$-$SiD_4$ | 56 - 70 | 68 | $Si_2D_6^+$ |
| | | 69 | $PD_2SiD_3^+$ |
| | | 70 | $P_2D_4^+$ |

formed simultaneously with the decomposition of the substrates. Moreover, $SiH_4$ disappears simultaneously and at rates comparable with those for the disappearance of $PH_3$, although $PH_3$ absorbs by far the major part (over 90%) of the incident radiation. The photolysis curves for the depletion of $PH_3$ and $SiH_4$ also indicate that the ratio of the rates of decomposition of both compounds is constant during photolysis. However, the ratios of the rates of product formation to the rates of depletion of substrates were constant only for the first few seconds of photolysis after which the products reached steady state concentrations. It can be seen in Fig. 3 that $H_2$ reached a steady state concentration before the irradiation was stopped and $P_2H_4$ and $Si_2H_6$ attained steady state concentrations even sooner; moreover, the concentrations of both $P_2H_4$ and $Si_2H_6$ began to fall slightly before the irradiation was stopped.

## 3.2. Quantum yields

Quantum yields for the depletion of substrates and for the formation of the volatile products are shown in Table 2. As may be seen, all quantum yields depend on the composition of reactant mixtures; comparable values are obtained in the photolyses of $PH_3$-$SiH_4$ and $PD_3$-$SiH_4$, as well as in those of $PH_3$-$SiD_4$ and $PD_3$-$SiD_4$.

The last four columns of Table 2 indicate the material balances obtained by consideration of only gaseous products. The amount of phosphorus in the reacted $PH_3$ that is accounted for by $P_2H_4$ and $PH_2SiH_3$ increases with decreasing partial pressure of $SiH_4$. The appropriate material balance values $\{2\Phi(P_2H_4) + \Phi(PH_2SiH_3)\}/\Phi(-PH_3)$ are in good agreement
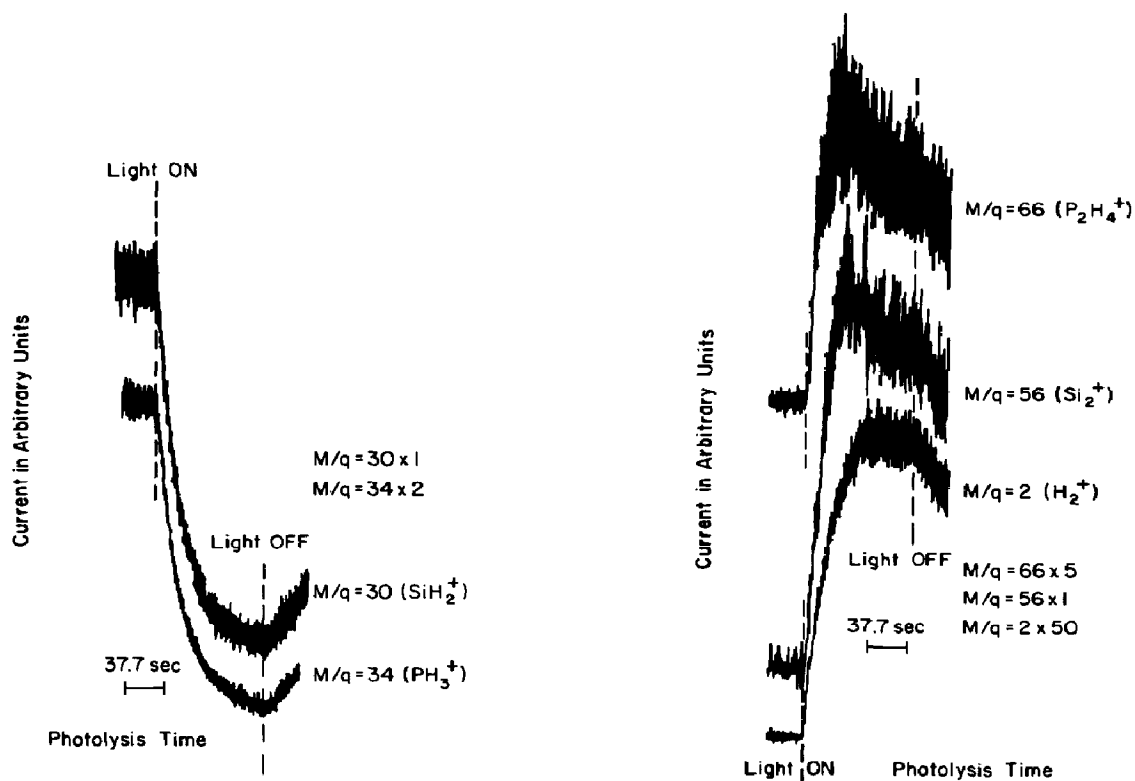
Fig. 2. Depletion of $PH_3$ ($m/q$ = 34) and $SiH_4$ ($m/q$ = 30) in the photolysis of $PH_3$–$SiH_4$ ($[PH_3]/[SiH_4]$ = 2).

Fig. 3. Formation of $H_2$ ($m/q$ = 2), $Si_2H_6$ ($m/q$ = 56) and $P_2H_4$ ($m/q$ = 66) in the photolysis of $PH_3$–$SiH_4$ ($[PH_3]/[SiH_4]$ = 2).

with those found earlier [1] for the 147 nm photodecomposition of pure $PH_3$. However, the amount of silicon that is accounted for by $Si_2H_6$ and $PH_2SiH_3$ decreases with decreasing partial pressure of $SiH_4$ and reaches a plateau at about 30%. This parallels earlier results [2] in that during the 147 nm photolysis of $SiH_4$ the gaseous products accounted for nearly 100% of silicon at $p(SiH_4)$ = 4 Torr; however, the amount of silicon atoms accounted for by gaseous products was significantly lower at lower partial pressures of $SiH_4$.

The dependences of all quantum yields on the partial pressure of $SiH_4$ in the photolysis of $PH_3$–$SiH_4$ are presented in Figs. 4 and 5. These relations will be discussed in Section 4.3.

### 3.3. Formation of the solid deposit

Solid substances formed on the walls of the photolysis cell and on the window of the lamp are seen directly as a white or light-yellow deposit. This deposit on the window of the lamp causes a decrease in the flux of the incident radiation as shown in Fig. 1. For all the systems investigated the

**TABLE 2**

Quantum yields in the photodecomposition of $PH_3(PD_3)$–$SiH_4(SiD_4)$ systems at 147 nm [a]

| Reactive gases | Pressure (Torr) | $\Phi(-PH_nD_{3-n})$ | | | $\Phi(-SiH_nD_{4-n})$ | | | $\Phi(H_2)$ | $\Phi(HD)$ | $\Phi(D_2)$ | $\Phi(P_2H_nD_{4-n})$ | | | $\Phi(Si_2H_nD_{6-n})$ | | | $\Phi(PSiH_nD_{5-n})$ | | | $(2\Phi_{III}+\Phi_V)/\Phi_I$ | $(2\Phi_{IV}+\Phi_V)/\Phi_{II}$ | Composition of the solid deposit | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | n | m/q[b] | $\Phi_I$ | n | m/q[b] | $\Phi_{II}$ | | | | n | m/q[b] | $\Phi_{III}$ | n | m/q[b] | $\Phi_{IV}$ | n | m/q[b] | $\Phi_V$ | | | x (for $PSiH_x)P_4(s)$ + $SiH_y)$ | y (for $SiH_y)$ |
| $PH_3$ | 0.48 | 3 | 34 | 1.9 | | | | 3.6 | — | — | 4 | 66 | 0.15 | | | | | | | 0.23 | | 0.14 | 0.53 |
| $SiH_4$ | 0.24 | | | | 4 | 30 | 1.0 | | | | | | | 6 | 56 | 0.16 | 5 | 60 | 0.13 | | 0.45 | | |
| $PH_3$ | 0.48 | 3 | 34 | 2.0 | | | | 3.7 | — | — | 4 | 66 | 0.14 | | | | | | | 0.21 | | 0.21 | 0.81 |
| $SiH_4$ | 0.224 | | | | 4 | 30 | 1.0 | | | | | | | 6 | 56 | 0.15 | 5 | 60 | 0.13 | | 0.43 | | |
| $PH_3$ | 0.48 | 3 | 34 | 2.0 | | | | 3.4 | — | — | 4 | 66 | 0.18 | | | | | | | 0.22 | | 0.17 | 0.81 |
| $SiH_4$ | 0.16 | | | | 4 | 30 | 0.76 | | | | | | | 6 | 56 | 0.13 | 5 | 60 | 0.080 | | 0.45 | | |
| $PH_3$ | 0.48 | 3 | 34 | 2.1 | | | | 3.2 | — | — | 4 | 66 | 0.22 | | | | | | | 0.24 | | 0.31 | 1.65 |
| $SiH_4$ | 0.12 | | | | 4 | 30 | 0.61 | | | | | | | 6 | 56 | 0.086 | 5 | 60 | 0.066 | | 0.39 | | |
| $PH_3$ | 0.48 | 3 | 34 | 2.2 | | | | 3.1 | — | — | — | | | | | | | | | — | | — | |
| $SiH_4$ | 0.08 | | | | 4 | 30 | 0.42 | | | | | | | 6 | 56 | 0.053 | 5 | 60 | 0.040 | | 0.35 | | |
| $PH_3$ | 0.48 | 3 | 34 | 2.5 | | | | 3.0 | — | — | — | | | | | | | | | — | | — | |
| $SiH_4$ | 0.053 | | | | 4 | 30 | 0.31 | | | | | | | 6 | 56 | 0.036 | 5 | 60 | 0.037 | | 0.35 | | |
| $PH_3$ | 0.48 | 3 | 34 | 2.7 | | | | 3.0 | — | — | — | | | | | | | | | — | | — | |
| $SiH_4$ | 0.04 | | | | 4 | 30 | 0.24 | | | | | | | 6 | 56 | 0.020 | 5 | 60 | 0.031 | | 0.30 | | |
| $PH_3$ | 0.48 | 3 | 33 | 1.6 | | | | 2.5 | 0.50 | 0.61 | — | | | | | | | | | — | | — | |
| $SiD_4$ | 0.224 | | | | 0 | 30 | 0.63 | | | | | | | 0 | 56 | 0.10 | — | | | | — | | |
| $PD_3$ | 0.48 | 0 | 37 | 1.9 | | | | 1.1 | 1.4 | 1.0 | — | | | | | | | | | — | | — | |
| $SiH_4$ | 0.224 | | | | 4 | 30 | 1.0 | | | | | | | 6 | 56 | 0.18 | — | | | | — | | |
| $PD_3$ | 0.48 | 0 | 37 | 1.4 | | | | — | 1.1 | 2.2 | — | | | | | | | | | — | | — | |
| $SiD_4$ | 0.224 | | | | 0 | 30 | 0.62 | | | | | | | 0 | 56 | 0.10 | — | | | | — | | |

Diluent gas, neon; total pressure, 40 Torr; light intensity, $5 \pm 0.5$ photons s$^{-1}$.

[a]Each quantum yield value in the table is the mean of at least five replicate experiments. In each case the ratio of the standard deviation to the appropriate mean value was less than 0.1.

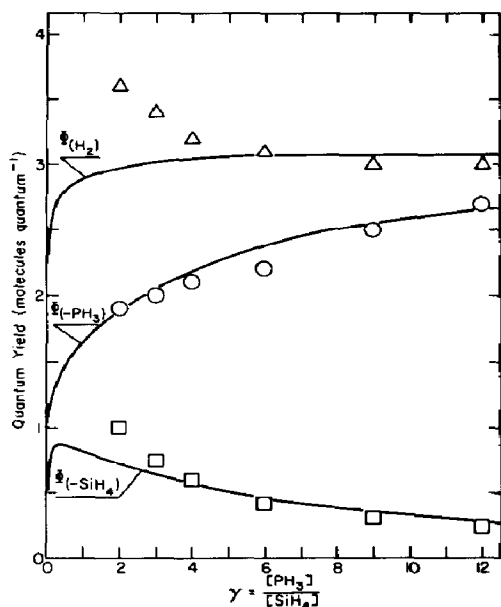[b]Ion chosen for the quantitative estimation.

Fig. 4. Dependence of quantum yields on $\gamma$ in the photolysis of $PH_3$–$SiH_4$ ($p(PH_3)$ = 0.48 Torr): ○, $\Phi(-PH_3)$; □, $\Phi(-SiH_4)$; △, $\Phi(H_2)$.
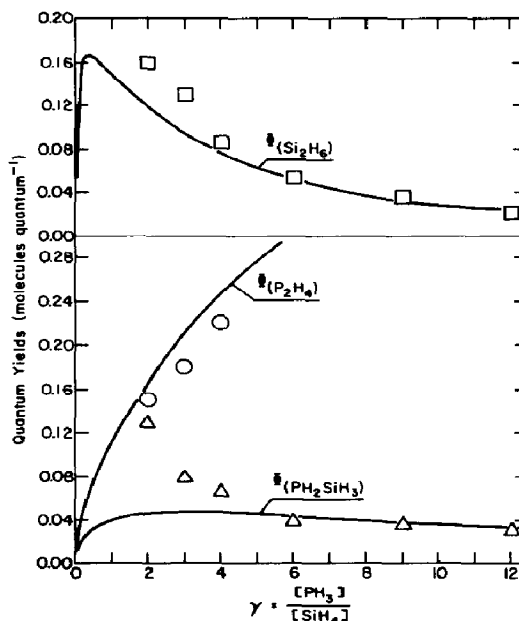
Fig. 5. Dependence of quantum yields on $\gamma$ in the photolysis of $PH_3$–$SiH_4$ ($p(PH_3)$ = 0.48 Torr): ○, $\Phi(P_2H_4)$; □, $\Phi(Si_2H_6)$; △, $\Phi(PH_2SiH_3)$.

amount of deposit increases with time of irradiation; the amount of deposit depends also on the composition of the reactant mixture. The rate of build-up of the deposit decreases in the following order: $PH_3$ > $PH_3$–$SiH_4$ > $PH_3$–$SiD_4$. The same trend is observed for depletion of $PH_3$ and $SiH_4$ (or $SiD_4$), based on our previous investigations [1] and on the data in Table 2. Because in all experiments the partial pressure of $PH_3$ was the same and because it absorbs by far the largest part of the incident radiation, the relative differences in rates of formation of the deposit are caused predominantly by differences in the rates of secondary processes in which $SiH_4$ (or $SiD_4$) participates.

The composition and structure of the solid deposits have not been studied. However, based on material balances of gaseous reactants we conclude that the deposits are mixtures of phosphorus and P–Si hydrides. Consideration of the following two distinct cases leads to the $x$ and $y$ values listed in Table 2: (i) formation of $PSiH_x$ as the solid product; (ii) formation of $P_4(s)$ and $SiH_y$ in the solid deposit. These values are in good agreement with those found in the photolysis of $PH_3$ [1] ($x$ = 0.2 - 0.7 in $PH_x$) and $SiH_4$ [26] ($x$ = 0.48 - 0.91 in $SiH_x$). The presence of phosphorus in the deposits was supported by performing mercury-photosensitized photolyses of $H_2$ or $D_2$ in a cell the walls of which were previously covered with the solid products of the 147 nm photolyses of the reactant mixtures listed in Table 2. Under these conditions only $PH_3$ or $PD_3$ were found in the gas phase [1].

## 4. Discussion

### 4.1. Nature of reaction intermediates

The photochemistry of two-component systems is not an easy problem for investigation. Firstly, the primary photodecomposition of both substrates can occur, which usually gives twice as many intermediate species as in a one-component system. Furthermore, quantum yield measurements become more difficult because it is hard to estimate exactly the amounts of photons absorbed by each component. Since more primary intermediate species appear, many additional pathways for secondary processes become available and this leads to difficulties in searching for adequate reaction mechanisms.

In the work described here all experiments were conducted under conditions such that $PH_3$ was in a sufficiently large excess that absorption of light by $PH_3$ accounted for 90% or more of the total radiation absorbed. Then we assumed as a reasonable approximation that the amounts of primary photodecomposition products of $SiH_4$ could be neglected in mechanistic considerations.

Our previous investigation [1] of the 147 nm photolyses of $PH_3$ and $PD_3$ enable us to assume three reactions, processes (1) - (3), as adequately describing the primary processes in the $PH_3-SiH_4$ system under our conditions, i.e.

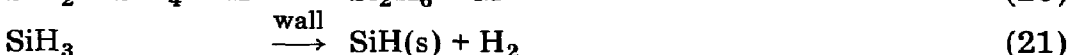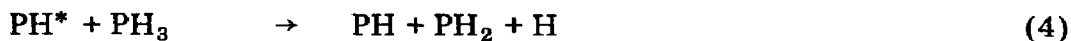$$PH_3 + h\nu \xrightarrow{\phi_a} PH^* + H_2 \tag{1}$$

$$PH_3 + h\nu \xrightarrow{\phi_b} PH_2^* + \dot{H} \tag{2}$$

$$PH_3 + h\nu \xrightarrow{\phi_c} PH + 2H \tag{3}$$

where $\phi$ is a primary quantum yield and $PH^*$, $PH_2^*$ and $PH$ indicate the primary photofragments with estimated excitation energies of 589.5 kJ $mol^{-1}$, 470.0 kJ $mol^{-1}$ and 156.9 kJ $mol^{-1}$ respectively [17].

### 4.2. Mechanism of the photolysis

The sum of the quantum yields for the disappearance of substrates (see Table 2) in the photodecomposition of $PH_3-SiH_4$ changes with $\gamma$ from 3.1 to about 2.6. These values are slightly lower than those found in the 147 nm photolysis of pure $PH_3$ [1]. However, this fact indicates that the reaction scheme proposed in the 147 nm photodecomposition of $PH_3$ [1] should also be valid for the present two-component system. The presence of $SiH_4$ in the reaction mixture creates new pathways for consumption of the primary photofragments and for the other secondary processes. Some must be identical with those shown to be important in the 147 nm photolysis of $SiH_4$ [2].

After consideration of many possible mechanisms subsequent to reactions (1) - (3), we propose those shown by reactions (4) - (21) as representing the most satisfactory description of the 147 nm photolysis of $PH_3-SiH_4$ mixtures for $[PH_3]/[SiH_4] > 4$:

$$PH^* + PH_3 \quad \rightarrow \quad PH + PH_2 + H \tag{4}$$

$$PH^* + PH_3 \quad \rightarrow \quad PH + PH_3 \tag{5}$$

$$PH^* \quad \rightarrow \quad PH + h\nu \tag{6}$$

$$PH_2^* + PH_3 \quad \rightarrow \quad PH_2 + PH_3 \tag{7}$$

$$PH_2^* \quad \rightarrow \quad PH_2 + h\nu \tag{8}$$

$$H + PH_3 \quad \rightarrow \quad H_2 + PH_2 \tag{9}$$

$$PH + PH \quad \xrightarrow{\text{wall}} \quad P_2(s) + H_2 \tag{10}$$

$$PH_2 \quad \xrightarrow{\text{wall}} \quad PH(s) + H \tag{11}$$

$$PH_2 + PH_2 + M \quad \rightarrow \quad P_2H_4 + M \tag{12}$$

$$PH^* + SiH_4 \quad \rightarrow \quad PH + SiH_4 \tag{13}$$

$$PH_2^* + SiH_4 \quad \rightarrow \quad PH_2 + SiH_4 \tag{14}$$

$$H + SiH_4 \quad \rightarrow \quad H_2 + SiH_3 \tag{15}$$

$$PH_2 + SiH_3 + M \quad \rightarrow \quad PH_2SiH_3 + M \tag{16}$$

$$SiH_3 + SiH_3 + M \quad \rightarrow \quad Si_2H_6 + M \tag{17}$$

$$SiH_3 + SiH_3 \quad \rightarrow \quad SiH_2 + SiH_4 \tag{18}$$

$$SiH_2 + PH_3 + M \quad \rightarrow \quad PH_2SiH_3 + M \tag{19}$$

$$SiH_2 + SiH_4 + M \quad \rightarrow \quad Si_2H_6 + M \tag{20}$$

$$SiH_3 \quad \xrightarrow{\text{wall}} \quad SiH(s) + H_2 \tag{21}$$

Efficient collisional quenching of emission from $PH^*$ by $PH_3$ has been demonstrated by many workers [1]. Since the radiation energy emitted, namely 347.8 kJ mol$^{-1}$ [17], is in excess of the average P—H bond energy in $PH_3$ [27], we assume that quenching processes may be accompanied by dissociation and we write reactions (4) and (5) to describe this. In contrast, collisional quenching of $PH_2^*$ by both $PH_3$ (reaction (7)) and $SiH_4$ (reaction (14)) as well as collisional quenching of $PH^*$ by $SiH_4$ (reaction (13)) cannot supply sufficient energy to dissociate molecules of substrates [17, 27, 28]. Reactions (9) [29, 30] and (15) [28, 31] have been found to be so fast that under our experimental conditions other processes of hydrogen atoms cannot compete with them. Reactions (6) and (8) simply describe the luminescence from $PH^*$ and $PH_2^*$ [1].

Energetic considerations based on the standard enthalpies of formation of the reactants [17, 32] indicate that the only energetically feasible reaction of PH is insertion into $PH_3$ to form $P_2H_4$; however, our earlier study [1] indicated that this reaction is not significant. Therefore we assume that PH does not react with either substrate in the gas phase. We propose reaction (10), which probably occurs on the walls of the photolysis cell, to describe the consumption of PH species [1].

Most of the phosphorus and silicon lost from the gas phase during photolysis must appear in the solid film produced, since only $P_2H_4$, $PH_2SiH_3$ and $Si_2H_6$ are observed in the gas phase and the yields are too low to account for all the phosphorus and silicon reacted. Therefore, reactions (11) for $PH_2$ [1] and (21) for $SiH_3$ [2] are proposed to account for this fact.

Reactions (12) and (16), which describe coupling of $PH_2$ radicals and the combination of $PH_2$ and $SiH_3$ radicals, are proposed on the basis of our previous study [1] as well as on the basis of the experimental facts of this investigation. The additional pathways (17) and (18) for consumption of $SiH_3$ radicals must be expected as these reactions were observed in the 147 nm photolysis of pure $SiH_4$ [2]. Finally, the formation of $Si_2H_6$ via insertion of $SiH_2$ into $SiH_4$ molecules (reaction (20)) and the formation of $PH_2SiH_3$ via insertion of $SiH_2$ into $PH_3$ molecules (reaction (19)) have to be expected to occur on the basis of our experimental results as well as on the basis of kinetic [2, 33] and thermodynamic [34] considerations.

## 4.3. Kinetic treatment of the mechanism

A standard steady state kinetic treatment of the mechanism described by eqns. (1) - (21) leads to cumbersome expressions which are presented in Appendix A. These expressions describe the dependences of all quantum yields on the composition $\gamma$ of the reactant mixture. Thus a trial-and-error procedure could be used for fitting the proposed mechanism to the experimental data. Numerical values of some of the parameters in expressions (A1) - (A12) could be assumed based on literature data. Thus, $\phi_a$, $\phi_b$, $k_5/k_4$ and $k_{11}^2/k_{12}[M]$ were taken from our previous report [1]: 0.8, 0.1, 1.1 and $1.6 \times 10^{14}$ molecules $cm^{-3}$ $s^{-1}$ respectively. $k_6/k_4$ was estimated from the measured luminescence lifetime of $PH^*$ and the quenching cross section [35] to be $4.3 \times 10^{15}$ molecules $cm^{-3}$. $k_{17}[M]/k_{18}$ was taken from the work of Reimann et al. [36] to be 1.43.

Using the values just reported and choosing values of $k_{15}/k_9$, $k_{13}/k_4$, $k_{16}[M]/k_{11}$, $q/k_{18}$, $k_{21}/k_{18}$ and $k_{19}/k_{20}$ to give the best overall fit to the experimental data at $[PH_3]/[SiH_4] > 4$, we plotted the derived quantum yields as functions of the composition of the reaction mixture in Figs. 4 and 5. Variation in the aforementioned parameters is not completely free as some of the values are subject to the following restrictions. The ratio $k_{15}/k_9$ was found to be 1.3, based on rate constants reported for reactions of hydrogen atoms with $SiH_4$ [31] and $PH_3$ [30]. $k_{18}$ should be less than $10^{-10}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ based on collision theory and information available about the rate constants for other similar systems, e.g. combination of $NH_2$ [37] and combination and disproportionation of alkyl radicals [38 - 40]. For the same reason $k_{16}[M]$ must also be less than $10^{-10}$ $cm^3$ molecule$^{-1}$ $s^{-1}$. For reactions (11) and (21) rate constants for diffusion to the wall of the order of 20 $s^{-1}$ are predicted using gas kinetic theory.

Based on these considerations the best fit was found for the following values of the parameters: $k_{15}/k_9 = 2.7$; $k_{13}/k_4 = 0.1$; $k_{16}[M]/k_{11} = 1.1 \times 10^{-13}$ $cm^3$ molecule$^{-1}$; $q/k_{18} = 2.8 \times 10^{24}$ photons molecules $cm^{-6}$; $k_{21}/k_{18} =$

$2.4 \times 10^{12}$ molecules $cm^{-3}$; $k_{19}/k_{20} = 0.1$. As may be seen in Figs. 4 and 5, the quantum yields derived from the mechanism are in reasonable agreement with the experimental results for $[PH_3]/[SiH_4] > 4$. The mechanism fails, however, at lower values of $\gamma$ and we believe that this failure is caused mainly by the availability of other reaction channels for $SiH_4$, *i.e.* primary photodecomposition. Assuming $q = 1.3 \times 10^{14}$ photons $cm^{-3}$ $s^{-1}$ (see Table 2) and $k_{17}[M]/k_{18} = 1.43$ [36] the results permit us to estimate the rate constants for reactions (18), (17) and (21). These estimates are $k_{18} = 4.6 \times 10^{-11}$ $cm^3$ molecule$^{-1}$ $s^{-1}$, $k_{17}[M] = 6.6 \times 10^{-11}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ and $k_{21} = 1.1 \times 10^2$ $s^{-1}$. To our knowledge the absolute rate constant values for disproportionation (reaction (18)) and combination (reaction (17)) of silyl radicals have not been mentioned in the literature as yet. However, the fact that the values of rate constants estimated by us for these two processes are very close to those reported for the analogous reactions of alkyl radicals [38 - 40] tends to confirm the basic correctness of the mechanism.

Taking $k_{15}/k_9 = 2.7$ and the rate constant for the reaction of hydrogen atoms with $SiH_4$ to be $4.3 \times 10^{-13}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ [31], the rate constant for the reaction of hydrogen atoms with $PH_3$ is estimated as $k_9 = 1.6 \times 10^{-13}$ $cm^3$ molecule$^{-1}$ $s^{-1}$. This value is about one-half of that reported by Lee *et al.* [30].

From our estimation it follows that the reactivity of $SiH_2$ toward $SiH_4$ is about 10 times higher than that toward $PH_3$ which is in good agreement with a report by Sefcik and Ring [41]. However, $PH_3$ is a more efficient quencher than $SiH_4$ toward PH* species.

In the high pressure limit of the partial pressure of $SiH_4$ all secondary processes involving $PH_3$ are negligible and $\Phi(-PH_3) \to 1$. However, at the limit of zero partial pressure of $SiH_4$, only reactions of $PH_3$ with species derived from $PH_3$ should occur. The mechanism proposed allows the following quantum yields to be predicted as $\gamma \to \infty$: $\Phi(-PH_3) = 3.1$; $\Phi(H_2) = 3.0$; $\Phi(P_2H_4) = 0.54$; $\Phi(-SiH_4) = 0$; $\Phi(Si_2H_6) = 0$; $\Phi(PH_2SiH_3) = 0$. The values of quantum yields for depletion of $PH_3$ and formation of $H_2$ and $P_2H_4$ as $\gamma \to \infty$ are in good agreement with the values reported earlier [1] in the 147 nm photodecomposition of pure $PH_3$.

The experimental and derived dependences of $\Phi(-PH_3)$ and $\Phi(-SiH_4)$ on light intensity at $\gamma = 2$ are shown in Fig. 6. The full curves were obtained using eqns. (A1) and (A2) and the values of the parameters mentioned earlier for the best fit. Similar dependences were found for $\Phi(H_2)$. From eqns. (A4), (A5) and (A6) increases in the quantum yields for the formation of $P_2H_4$, $Si_2H_6$ and $PH_2SiH_3$ are predicted with an increase in the incident light intensity; however, our experimental results show decreases in all these quantum yields with an increase in incident light intensity. The thermal decomposition of these compounds should not play a significant role in our experiments, as was found previously for $P_2H_4$ [1]. The most probable explanation of these discrepancies is that photodecomposition of gaseous phosphorus and silicon hydrides is influencing our measurements. The influence, which would act to reduce the measured quantum yields, would become stronger as the light intensity is increased.
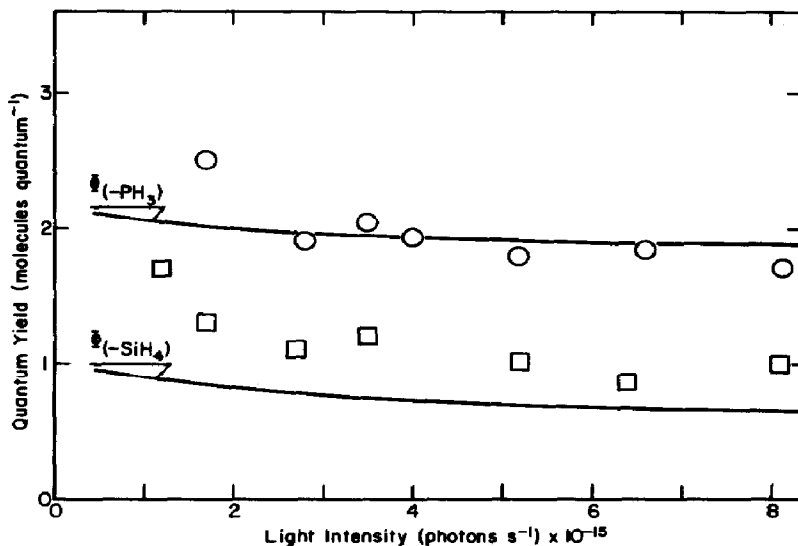
Fig. 6. Dependence of quantum yields on the light intensity in the photolysis of $PH_3$–$SiH_4$ ($[PH_3]/[SiH_4] = 2$).

The reaction scheme proposed might be useful for the qualitative explanation of relative differences in quantum yields in the case where deuterated reactants were used. It is known from our previous report [1] that on photodecomposition of $PD_3$ primary processes (2) and (3) have higher quantum yields. This means that during the photodecomposition of $PD_3$-containing systems larger amounts of deuterium atoms should appear compared with the amounts of hydrogen atoms following photodecomposition of $PH_3$-containing systems. In contrast, $PD_3$ and probably also $SiD_4$ are more efficient quenchers of excited $PH^*$ or $PD^*$ species than $PH_3$ and $SiH_4$ are [1]. Furthermore, the rate constants for reactions of hydrogen atoms with reactants should be lower when P—D or Si—D bonds are broken [1, 31]. These three effects are responsible for differences in the quantum yields which are shown in Table 2.

Our experimental results indicate clearly that the PH molecules formed in the 147 nm photolysis of $PH_3$ do not participate in insertion processes with molecules of $PH_3$ or $SiH_4$; a similar behavior of PH was observed earlier [1]. This anomalous behavior probably arises from the fact that PH is formed mainly in triplet states in the 147 nm photolysis of $PH_3$ [17, 35, 42 - 44]; insertion processes can take place only with singlet PH. However, $SiH_2$ species are formed in singlet states following flash photolysis of $SiH_4$ [45] and so silylene radicals may easily undergo insertion reactions with molecules of substrates. This is fully supported by the experimental data of this study as well as by previously reported observations [1, 2].

The complete mechanism of the photolysis of $PH_3$–$SiH_4$ mixtures is undoubtedly more complicated than that shown by reactions (1) - (21). Nevertheless, the agreement obtained between the experimental quantum

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yields and those derived from the mechanism suggests that the approach proposed is a good approximation for description of the vacuum UV photochemistry of the $PH_3$-$SiH_4$ system.

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## Appendix A

A standard steady state treatment of the mechanism depicted by reactions (1) - (21) (see text) leads to the following expressions for the quantum yields for the depletion of substrates and the formation of products:

$$\Phi(-PH_3) = 1 + \frac{\phi_a}{B} + \frac{C+E}{A} + \frac{k_{19}}{k_{20}} F^2 \left\{ 2\frac{q}{k_{18}} \left( \frac{1}{\gamma} + \frac{k_{19}}{k_{20}} \right) \right\}^{-1} \tag{A1}$$

$$\Phi(-SiH_4) = \frac{k_{15}}{k_9}(C+E)(\gamma A)^{-1} + \frac{F^2}{2q/k_{18}} \left( \frac{1}{1 + \gamma k_{19}/k_{20}} - 1 \right) \tag{A2}$$

$$\Phi(H_2) = 0.5 + \phi_a - 0.5\phi_b + C + E + \frac{k_{21}F/k_{18}}{q/k_{18}} \tag{A3}$$

$$\Phi(P_2H_4) = \frac{1}{2}\left[ \left\{ \frac{1}{4}\frac{k_{11}^2}{qk_{12}[M]} \left( 1 - \frac{1}{A} \right)^2 + D \right\}^{1/2} - \frac{1}{2}\frac{k_{11}^2}{qk_{12}[M]} \left( 1 - \frac{1}{A} \right) \right]^2 \tag{A4}$$

$$\Phi(Si_2H_6) = \frac{F^2}{2q/k_{18}} \left( \frac{k_{17}[M]}{k_{18}} + \frac{1}{1 + \gamma k_{19}/k_{20}} \right) \tag{A5}$$

$$\Phi(PH_2SiH_3) = F\left\{ \frac{k_{16}[M]}{k_{11}}E + \frac{k_{19}/k_{20}}{2q/k_{18}(1/\gamma + k_{19}/k_{20})} \right\} \tag{A6}$$

Here $\gamma$ is the ratio $[PH_3]/[SiH_4]$ of the reactants, $q$ represents the incident light intensity and

$$A = 1 + \frac{k_{15}}{k_9}\frac{1}{\gamma} \tag{A7}$$

$$B = 1 + \frac{k_5}{k_4} + \frac{k_6}{k_4[\text{PH}_3]} + \frac{k_{13}}{k_4} \frac{1}{\gamma} \tag{A8}$$

$$C = 2 - 2\phi_a - \phi_b + \frac{\phi_a}{B} \tag{A9}$$

$$D = \phi_b + \frac{\phi_a}{B} + \frac{C}{A} \tag{A10}$$

$$E = \left\{ \frac{1}{4} \left( \frac{k_{11}^2}{qk_{12}[\text{M}]} \right)^2 \left( 1 - \frac{1}{A} \right)^2 + \frac{k_{11}^2}{qk_{12}[\text{M}]} D \right\}^{1/2} - \frac{1}{2} \frac{k_{11}^2}{qk_{12}[\text{M}]} \left( 1 - \frac{1}{A} \right) \tag{A11}$$

$$F = \left\{ \frac{1}{4} \left( \frac{k_{16}[\text{M}]qE/k_{11}k_{18} + k_{21}/k_{18}}{k_{17}[\text{M}]/k_{18} + 1} \right)^2 + \frac{k_{15}q(C + E)/k_9 k_{18}}{\gamma A (k_{17}[\text{M}]/k_{18} + 1)} \right\}^{1/2} -$$
$$- \frac{1}{2} \frac{k_{16}[\text{M}]qE/k_{11}k_{18} + k_{21}/k_{18}}{k_{17}[\text{M}]/k_{18} + 1} \tag{A12}$$