## **Decomposition Kinetics of a Static Direct Current Silane Glow Discharge**

## P. A. Longeway,\* R. D. Estes, and H. A. Weakliem

RCA Laboratories, Princeton, New Jersey 08540 (Received: March 31, 1983)

We have studied the decompositon kinetics of a static dc silane discharge using mass spectrometric techniques. The principal neutral products observed were hydrogen, disilane, trisilane, trace amounts of higher silanes, and nonstoichiometric silicon hydride solids. The initial rates of formation of the products and depletion of the silane were measured and found to be independent of silane pressure and had a linear dependence on the discharge current. Nitric oxide, a known free-radical scavenger, was introduced into the discharge to determine the relative yields of SiH<sub>3</sub> and SiH<sub>2</sub>. The primary decomposition was found to proceed approximately 80-90% to the silyl radical, SiH<sub>3</sub>. The effects of NO addition were the reduction in the formation rate of disilane and trisilane and almost total suppression of solid formation. We propose a mechanism which includes both ion and neutral radical reactions and conclude that the major decomposition processes lead to  $SiH_3$  and  $SiH_3$ . Kinetic treatment of the mechanism gave values for the product yields that were in good agreement with the observed yields.

## Introduction

Gaseous polysilane, nonstoichiometric  $SiH_x$  powders, and amorphous hydrogenated silicon films may all be produced in a silane glow discharge. The discharge operating conditions and the physical properties of surfaces in contact with the discharge determine the relative amounts of the products which are produced. Previous studies on the decomposition of silane have employed UV photolysis,<sup>1</sup> Hg photosensitization,<sup>2</sup>  $\gamma$ -ray irradiation,<sup>3</sup> infrared multiphoton excitation,<sup>4</sup> hydrogen atom initiation,<sup>5</sup> and thermal excitation.<sup>6</sup> Ion-molecule reactions have also been studied by tandem mass spectroscopy<sup>7</sup> and by ion cyclotron resonance.<sup>8</sup> Several reaction pathways involving both radicals and ions leading to various products have been deduced from these earlier studies.<sup>1-8</sup> We wished to determine the dominant reactions in the glow discharge decomposition of pure silane and have therefore studied the kinetics using mass spectroscopic detection of the reactant and the principal stable, neutral products in a static dc excited glow discharge.

The glow discharge is initiated and maintained by electron and ion impact processes with silane and the electrodes which result in the production of electrons, ions, and radicals. Subsequent reactions may proceed via either an ionic or a radical sequence to produce the higher silanes and various forms of solid product. In the present case, the products are produced predominantly by the radical pathway.

We shall describe the result of the determination of the initial reaction rates of SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, Si<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub> in static dc silane glow discharges. The addition of NO to silane glow discharges was found to inhibit the production of Si<sub>2</sub>H<sub>6</sub>, Si<sub>3</sub>H<sub>8</sub>, and solid products,  $SiH_x$  where x usually lies in the range 0.05 to 0.30. The principal intermediates are SiH<sub>2</sub> and SiH<sub>3</sub> and the primary decomposition was found to yield approximately 80-90% SiH<sub>3</sub>. A kinetic analysis of the ionic and free radical reaction sequences gave values for the product yields which were in good agreement with the observed yields.

#### **Experimental Section**

The dc glow discharges were ignited at room temperature in a stainless steel, 98-L, vacuum chamber. One wall of the chamber was equipped with a removeable aperture disk separating it from a dual-differentially pumped quadrupole mass spectrometer system (Extranuclear Laboratories, Inc.).<sup>9</sup> The gaseous species to be

mass analyzed from the discharge chamber were transformed into a molecular beam by the aperture in the chamber wall and a second aperture separating the two pumping stages. The first and second apertures (200 and 1000  $\mu$ m, respectively), maintained both mass spectrometer chambers at or below  $1 \times 10^{-5}$  torr. The sampling (first) aperture was located in the plane of one of the electrodes and was thus close to the glow discharge. The ion source was located immediately behind the second aperture which, in turn, was 5 cm from the first aperture, consequently the gas suffered no collisions during its passage from the discharge chamber to the ion source region. The ion source was an open design consisting of a tungsten filament outlining a square centered about the line formed by the quadrupole axis and the two apertures. This configuration ensured line-of-sight sampling from the discharge.

The discharge chamber was filled with silane to initial pressures,  $p_0$ , in the range 0.25–0.75 torr, as measured with a capacitance manometer gauge (MKS Baratron, Model 310). Glow discharges were operated with dc currents in the range 10-80 mA. The reactant and product gases were monitored by tuning the quadrupole mass filter to particular values of m/e and measuring the ion current as a function of time after igniting the discharge. We used the mass peaks m/e 2 for hydrogen, m/e 32 for silane, m/e62 for disilane, and m/e 92 for trisilane. There is minimal interference from fragments produced by electron impact ionization of the higher silanes at the values m/e 32 and 62. The sensitivity of the mass spectrometer system was directly measured for H<sub>2</sub>,  $SiH_4$ , and  $Si_2H_6$ . This was done by measuring the output current at the appropriate m/e value for various pressures of H<sub>2</sub>, SiH<sub>4</sub>, and  $Si_2H_6$  in the large chamber, but with no discharge. Since trisilane was not available to us, we used an indirect procedure to obtain its sensitivity. We assume that the total ionization cross sections for the silanes  $Si_nH_{2n+2}$  have a dependence on *n* of the form  $Q_n = n^P Q_1$ , which we have found to accurately represent the values reported for the normal hydrocarbons,<sup>9</sup> using the value P= 0.84. We determined the relative transmission of the quadrupole as a function of m/e by comparison of the measured ion current with the known 70-eV fragmentation pattern of n-heptane. We then used the measured relative transmission together with the measured ion currents to obtain the ratio of the total ion currents  $I(Si_2H_6)/I(SiH_4) = 1.8$ , which gives P = 0.96. We obtained the sensitivity for trisilane by using the measured fragmentation pattern in the range m/e 84 to 92 and making the assumption that the fragmentation makes a negligible contribution to ion currents of m/e 62 and 32, together with the measured SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub> sensitivities and the value of P = 0.96.

The gases were all obtained from commercial sources and were used without further purification. The H<sub>2</sub>, SiH<sub>4</sub>, and NO were found to have a purity greater than 99.5% by mass spectroscopic analysis. The hydrogen was ultrahigh-purity grade and the NO

<sup>(1)</sup> G. G. A. Perkins, E. R. Austin, and F. W. Lampe, J. Am. Chem. Soc., 101, 1109 (1979).

<sup>(2)</sup> E. Kamaratos and F. W. Lampe, J. Phys. Chem., 74, 2267 (1970).
(3) J. F. Schmidt and F. W. Lampe, J. Phys. Chem., 73, 2706 (1969).
(4) P. A. Longeway and F. W. Lampe, J. Am. Chem. Soc., 103, 6813

<sup>(1981).</sup> 

<sup>(5)</sup> G. K. Moortgat, Thesis, University of Detroit, 1970.
(6) P. Neudorfl, A. Jodhan, and O. P. Strausz, J. Phys. Chem., 84, 338 (1980). (7) T.-Y. Yu, T. M. H. Cheng, V. Kempter, and F. W. Lampe, J. Phys.

Chem. 76, 3321 (1972).

<sup>(8)</sup> J. M. S. Henis, G. W. Stewart, M. K. Tripodi, and P. P. Gaspar, J. Chem. Phys., 57, 389 (1972).

<sup>(9)</sup> F. W. Lampe, J. L. Franklin, and F. H. Field, J. Am. Chem. Soc., 79, 6129 (1957).







Figure 2. Time dependence of  $SiH_4$ ,  $Si_2H_6$ ,  $Si_3H_8$ , and  $H_2$  in a static dc glow discharge.

was CP grade, both purchased from Matheson Co. The silane was TOPS grade purchased from Ideal Gas Products. Disilane of unstated purity was purchased both from Merck Co. and from Cambridge Isotope Laboratories. Mass spectroscopic examination showed them both to contain about 5% monosilane, 94% disilane, and less than 1% impurities.

## Results

Silane. When a glow discharge is ignited in a sealed chamber containing silane at an initial pressure,  $p_0$ , the following events occur. The pressure rises, rapidly at first, then slowly approaches a limit having a value somewhat less than  $2p_0$  and the color of the glow discharge emission changes from a deep blue to a pale pink. Mass spectroscopic measurements of the gas emerging from the glow discharge plasma shows that the silane concentration continuously decreases and finally vanishes and hydrogen, disilane, and trisilane are produced. The evolution of the hydrogen follows the general shape of the p vs. time curve but is not an exact replica. The disilane and trisilane reach a maximum intensity and then slowly decrease to zero as shown in Figure 1. After the discharge was extinguished and the chamber vented, a solid deposit is found on all surfaces of the chamber. Depending on the discharge conditions and the temperature of the surfaces, the solid may be a hard grey film or a yellow-brown powder. The ion currents corresponding to the concentrations of the products  $H_2$ ,  $Si_2H_6$ , and  $Si_3H_8$  depend linearly on time, as shown in Figure 2. The  $SiH_4^+$  (m/e 32) ion current, which is proportional to the SiH<sub>4</sub> concentration, has an initial linear decrease with time, as shown in Figure 2. The constant initial slope of the concentration vs.

TABLE I: Measured Fractional Rates for the Loss of SiH<sub>4</sub>, and the Formation of  $H_2$ ,  $Si_2H_6$ , and  $Si_3H_8$ 

compd	$f(\mathbf{x})$	compd	$f(\mathbf{x})$	-
SiH <sub>4</sub>	1.0	H <sub>2</sub>	0.69	-
Si <sub>2</sub> H <sub>6</sub>	0.39	solid a	0.13	
Si <sub>3</sub> H	0.03			

<sup>a</sup> Calculated from Si-atom balance.



Figure 3. Rate of formation of  $Si_2H_6$  and  $Si_3H_8$  relative to the corresponding rates with no NO added as functions of  $(p_{NO})^{-1}$ .

time curve is the initial rate of reaction, and we find that the initial silane depletion and product formation rates are independent of pressure in the range studied, and depend linearly on the dc discharge current. The fractional rates  $f(x) = R(x)/R(-SiH_4)$  are given in Table I, wherein R(x) is the observed rate of formation of species x and  $R(-SiH_4)$  is the observed depletion rate of silane.

*Nitric Oxide.* The addition of NO to SiH<sub>4</sub> is known to have a profound effect on the product formation resulting from silane decomposition.<sup>1</sup> Nitric oxide is a free radical and would be expected to react strongly with other free radicals. The addition of NO to a SiH<sub>4</sub> discharge adds the complication that NO may itself be decomposed to produce products capable of reacting with SiH<sub>4</sub> or its intermediate reaction products. We therefore examined a pure NO glow discharge by mass spectrometry. The steady-state composition of a glow discharge in NO at p = 0.5 torr, 0.2 mA cm<sup>-2</sup> is 86.4% NO, 6.7% O<sub>2</sub>, 6.7% N<sub>2</sub>, and 0.2% N<sub>2</sub>O. The fractional loss of NO is 18% in this case, therefore when added to a silane discharge we expect that 85–90% of the NO remains. No additional free radicals are produced and the only significant competing reaction is expected to be that of oxygen with silane

$$\mathrm{SiH}_4 + \mathrm{O}_2 \to \mathrm{SiO}_2 + 2\mathrm{H}_2 \tag{1}$$

The rate of formation of  $O_2$  was measured in NO discharges and was found to be too low to account for a significant loss of SiH<sub>4</sub> in SiH<sub>4</sub>/NO glow discharges.

Silane/Nitric Oxide Glow Discharges. The addition of NO to a monosilane glow discharge completely inhibits the production of SiH<sub>x</sub> solids and also causes a decrease in the yield of a Si<sub>2</sub>H<sub>6</sub> and Si<sub>3</sub>H<sub>8</sub>. Upon the addition of NO to a silane discharge, we find that no SiH<sub>x</sub> solid is formed; rather a transparent, whitish film is deposited. The infrared spectrum of this film shows the presence of both Si-H and Si-O bonds. A plot of the normalized fractional product rates of Si<sub>2</sub>H<sub>6</sub> and Si<sub>3</sub>H<sub>8</sub> vs. the reciprocal of the partial pressure of NO is shown in Figure 3. The data points fall on a straight line, which extrapolated to  $(P_{NO})^{-1} = 0$  gives the value for this rate for disilane equal to 0.09, and for trisilane the value is 0.21. Thus, under conditions of complete scavenging, the yield of disilane is 9% of that which would be produced under the same reaction conditions, but with no scavenging, and for trisilane 21% remains unscavenged.

Examination of the gaseous products of the  $SiH_4/NO$  glow discharges by mass spectrometry shows the presence of N<sub>2</sub>O and  $(SiH_3)_2O$  in nearly equal concentrations. These products are

Kinetics of a Static dc Silane Glow Discharge

produced by the overall reaction sequence

$$SiH_3 + NO \rightarrow SiH_3NO$$
 (2)

$$2(\text{SiH}_3\text{NO}) \rightarrow (\text{SiH}_3)_2\text{O} + \text{N}_2\text{O}$$
(3)

## **Kinetics and Mechanism**

*Primary Processes.* In order to develop a mechanistic model for the silane dc discharge, it was necessary to consider the types of primary decomposition reactions that could occur. Both ions and neutral radicals are known to exist as primary products in the plasma, hence, we have included both ion-molecule reactions and radical-molecule reactions.

The decomposition pathways for  $SiH_4$  which we propose for the DC plasma are

$$SiH_4 + e^- \rightarrow SiH_2 + H_2 + e^-$$
 (2.43 eV) (A)

$$SiH_4 + e^- \rightarrow SiH_3 + H + e^-$$
 (3.86 eV) (B)

$$SiH_4 + e^- \rightarrow SiH_2 + 2H + e^-$$
 (6.74 eV) (C)

$$SiH_4 + e^- \rightarrow SiH_2^+ + H_2 + 2e^-$$
 (11.9 eV) (D)

$$SiH_4 + e^- \rightarrow SiH_3^+ + H + 2e^-$$
 (12.3 eV) (E)

The 147-nm vacuum-UV photolysis of SiH<sub>4</sub> utilizes 8.44-eV photons and proceeds via reactions B and C, the quantum yields being 0.17 and 0.83, respectively.<sup>1</sup> On the other hand, the IR multiphoton decomposition<sup>4</sup> of SiH<sub>4</sub> utilizes 0.12-eV photons and proceeds almost exclusively (98%) via (A). In addition, the  $\gamma$ -ray radiolysis of SiH<sub>4</sub><sup>10</sup> has been shown to yield SiH<sub>2</sub><sup>+</sup> and SiH<sub>3</sub><sup>+</sup> as the most abundant primary ionic products. This is consistent with similar observations for the silane plasma.<sup>11,12</sup> We have therefore included reactions D and E as part of our proposed mechanism. Because the cross sections for reactions A, B, and C have not been measured, we can say little about the relative importance of reactions A through E.

The mean electron temperature,  $T_{\rm e}$ , of silane plasmas has been measured to be 0.5–5.0 eV.<sup>11,12</sup> Thus, ionization via (D) and (E) arises from the high-energy tail of the distribution and from the fast electrons which are accelerated across the negative glow without collision. Electron impact from lower energy electrons may give rise to vibrational excitation which has a cross section  $\sim 10^{-15}$  cm<sup>2</sup> near the threshold.<sup>13</sup> This may prove to be an important decomposition process for reactions A and B because of the relatively large number of low-energy electrons in the distribution. Photon excitation to a band of states near 8.3 eV has been assigned as the transition to the T<sub>2</sub> state,<sup>14</sup> so we may expect vertical excitation to this state would give rise to reactions B and C. We expect the cross section for the electronic excitation of SiH<sub>4</sub> to be close to that of CH<sub>4</sub> which has the known value<sup>15</sup> of  $10^{-16}$  cm<sup>2</sup>.

Mechanism. The primary intermediates arising from processes A through E are SiH<sub>2</sub>, SiH<sub>3</sub>, H, SiH<sub>2</sub><sup>+</sup>, and SiH<sub>3</sub><sup>+</sup>. We propose the following mechanism for the further reactions of these primary intermediates, in accordance with the scheme proposed for the UV photolysis of silane<sup>1</sup> and the  $\gamma$ -ray radiolysis of SiH<sub>4</sub>:<sup>10</sup>

$$H + SiH_4 \rightarrow SiH_3 + H_2 \tag{4}$$

$$\operatorname{SiH}_2 + \operatorname{SiH}_4 \to \operatorname{Si}_2 \operatorname{H}_6^* \tag{5}$$

$$\mathrm{SiH}_3 + \mathrm{SiH}_3 \rightarrow \mathrm{Si}_2\mathrm{H}_6^{**} \tag{6}$$

 $SiH_3 + SiH_3 \rightarrow SiH_2 + SiH_4$  (7)

$$Si_2H_6^* \rightarrow SiH_3SiH + H_2$$
 (8)

- (10) J. F. Schmidt and F. W. Lampe, J. Phys. Chem., 73, 2706 (1969).
  (11) H. A. Weakliem, "Third Symposium on Plasma Processing", J. Dielman, R. G. Frieser, and G. S. Mathad, Ed., Electrochemical Society, Pennington, 1982.
- (12) G. Turban, Y. Catherine, and B. Grolleau, Thin Solid Films, 67, 309 (1980).
- (13) G. Turban, Y. Catherine, and B. Grolleau, Plasma Chem. Plasma Proc., 2, 61 (1982).
  - (14) M. S. Gordon, J. Chem. Phys., 69, 4955 (1978).
  - (15) H. F. Winters, J. Phys. Chem., 63, 3462 (1975).

The Journal of Physical Chemistry, Vol. 88, No. 1, 1984 75

. . .

~ . . . .

$$S_{1_2}H_6^* + M \rightarrow S_{1_2}H_6 + M \tag{9}$$

~. --

$$Si_2H_6^{**} \rightarrow SiH_3SiH + H_2$$
(10)  
$$Si H ** \rightarrow SiH + SiH$$
(11)

$$\operatorname{Si_2H_6^{**}} + \operatorname{M} \to \operatorname{Si_2H_6} + \operatorname{M} \qquad (11)$$

$$Si_{2}I_{6} + Si_{4} \rightarrow Si_{3}H_{8}$$
(12)

$$2\mathrm{SiH}_3 \rightarrow \mathrm{Si}_2(\mathrm{S}) + 3\mathrm{H}_2 \tag{14}$$

$$\operatorname{SiH}_2^+ + \operatorname{SiH}_4 \to \operatorname{SiH}_3^+ + \operatorname{SiH}_3$$
(15)

$$\mathrm{SiH}_3^+ + \mathrm{SiH}_4 \rightleftharpoons \mathrm{Si}_2 \mathrm{H}_7^{+*} \tag{16}$$

Reaction 4 of H with SiH<sub>4</sub> is very rapid,<sup>16</sup> as is the insertion reaction 5 of SiH<sub>2</sub> into SiH<sub>4</sub>,<sup>17</sup> thus we assume that these are the sole reactions of H and SiH<sub>2</sub> under the conditions of these experiments. The symbol Si<sub>2</sub>H<sub>6</sub>\* denotes an activated disilane molecule having an excess energy of at least 49 kcal/mol,<sup>17</sup> whereas the symbol Si<sub>2</sub>H<sub>6</sub>\*\* denotes an activated molecule having at least 73 kcal/mol<sup>18</sup> excess energy.

Reaction 14 is clearly incomplete in that it neglects the role of a surface for the reaction to occur upon and implies no H-atom incorporation into the resulting solid material. Nevertheless, as will be seen, it serves well as a simple description of the film formation process. SiH<sub>3</sub> has been invoked as the sole solid-forming intermediate based on the observation that film formation was almost totally suppressed in the presence of NO, as mentioned earlier, and on the observation that similar results obtain upon the addition of NO to SiH<sub>4</sub> during the UV photolysis.<sup>1</sup> We do not suggest that SiH<sub>3</sub> is the only possible film-forming intermediate; simply that it appears to be the dominant one under our conditions.

Furthermore, reaction 15 is also very rapid<sup>19</sup> and we assume that this is the sole reaction of  $SiH_2^+$  under our conditions. Reaction 16 is included on the basis of the results of a study concerning the ion-molecule reactions of silane.<sup>7</sup> It was concluded that  $k_{-16}$  is much greater than the rate constant for any forward reaction of  $Si_2H_6^{+*}$ . It was also observed that the further reactions of  $Si_2H_7^{+*}$  gave rise to larger ionic clusters  $Si_xH_v^+$  via collisional stabilization; however, the rate constant for this reaction is  $\sim 10^{-26}$  $cm^{-3} mol^{-2} s^{-1}$ . We propose a similar fate for SiH<sub>3</sub><sup>+</sup> based on the observation<sup>20</sup> that there exists a correlation between the concentration of  $SiH_3^+$  in the plasma and the concentrations of the larger ionic clusters  $Si_x H_v^+$  (x = 2-5). Thus, we expect the major loss process for  $SiH_3^+$  to be recombination at the wall, which gives rise to SiH<sub>3</sub>. Based on these considerations and for purposes of the kinetic treatment which follows, we treat  $SiH_3^+$  as a chemically inert intermediate.

Kinetic Treatment of the Mechanism. Both Si<sub>2</sub>H<sub>6</sub> and Si<sub>3</sub>H<sub>8</sub> can be produced by SiH<sub>2</sub> or SiH<sub>3</sub>. In the presence of NO, one would observe only those higher silanes produced via SiH<sub>2</sub>. Hence, the unscavenged fraction of the value of  $[f(Si_2H_6) + f(Si_3H_8) +$  $1/_2f(solid)]$  would be the value for the fraction of the dissociative processes proceeding via (A) and (C). The values of  $f(Si_2H_6)$  and  $f(Si_3H_8)$  are reduced to 9% and 21% of their values in the absence of NO, respectively, as shown in Figure 3. As noted earlier, the value of f(solid) in the absence of NO is apparently reduced to zero in the presence of NO. Hence, the value of  $[f(Si_2H_6) +$  $f(Si_3H_8) + 1/_2f(solid)]$  in the presence of NO is only 9% of its value in the absence of NO. Reactions B and C each give rise to 2 SiH<sub>3</sub>, and reactions D and E each give rise to a single SiH<sub>3</sub>. Thus, we can express the ratio of the fractional extents of the primary processes as

 $(f_{\rm A} + f_{\rm C})/(f_{\rm B} + f_{\rm C} + 2f_{\rm D} + 2f_{\rm E}) = 0.09/0.91$ 

Although we are unable to assign the individual values for  $f_A$ 

- (1975). (19) T. M. Mayer and F. W. Lampe, J. Phys. Chem., 78, 2195 (1974).
- (20) J. Perrin, J. P. M. Schmitt, G. deRosny, B. Drevillon, J. Huc, and A. Lloret, Chem. Phys., 73, 383 (1982).

<sup>(16)</sup> E. R. Austin and F. W. Lampe, J. Phys. Chem., 81, 1134 (1977).
(17) P. John and J. H. Purnell, J. Chem. Soc., Faraday Trans. 1, 69, 1455

<sup>(1973).</sup> (18) P. Potzinger, A. Ritter, and J. Krause, Z. Naturforsch. A, 30, 347

through  $f_{\rm E}$ , clearly the SiH<sub>3</sub>-generating processes dominate. A recent estimate of the ratio of the cross section of dissociative ionization to dissociation to neutrals for silane assigns the value at  $0.5 \pm 0.1$ .<sup>20</sup> Since ion-molecule reactions are generally several orders of magnitude faster than radical-molecule reactions, it is reasonable to assume that a large fraction of the SiH<sub>3</sub> generated in the plasma arises via reaction 15. Thus, while SiH<sub>2</sub> generation (via processes A and C) is energetically favored, the kinetics of the processes seem to dominate, leading to an abundance of SiH<sub>3</sub>.

Using steady-state approximations for  $[SiH_3]^2$ ,  $[SiH_3SiH]$ ,  $[Si_2H_6^*]$ , and  $[Si_2H_6^{**}]$  and combining these with the standard rate equations for the product formations and SiH<sub>4</sub> depletion as derived from the proposed mechanism, we obtained the following expressions for the specific yields, Y(x). The relationship between the yield Y(x) and the experimentally measured reaction rate is given by the equation R(x)/i = mY(x) wherein *i* is the current in electrons per second. The factor *m* represents the electron multiplication produced by secondary emission and the other electron generation processes which take place to initiate and sustain a glow discharge. We shall introduce the definition  $\gamma = f_B + f_C + 2f_D + 2f_E$  in order to simplify the following expressions

$$Y(-SiH_4) = 2(f_A + f_B + 2f_C + f_D + f_E) + \left[\frac{k_8}{k_8 + k_9[M]}\right] \left[(f_A + f_C) + \gamma \left(\frac{k_7}{k_6 + k_7 + k_{14}}\right) + \left(\frac{k_6}{k_6 + k_7 + k_{14}}\right) \left(\frac{k_{11}}{k_{10} + k_{11} + k_{12}[M]}\right)\right] + \left(\frac{k_6}{k_6 + k_7 + k_{14}}\right) \left(\frac{k_{10}}{k_{10} + k_{11} + k_{12}[M]}\right) + \left(\frac{k_6}{k_6 + k_7 + k_{14}}\right) \left(\frac{k_{10}}{k_{10} + k_{11} + k_{12}[M]}\right) (I)$$

$$Y(\text{Si}_{2}\text{H}_{6}) = \left[\frac{k_{9}[\text{M}]}{k_{8} + k_{9}[\text{M}]}\right] \left[(f_{\text{A}} + f_{\text{C}}) + \gamma\left(\frac{k_{7}}{k_{6} + k_{7} + k_{14}}\right) + \gamma\left(\frac{k_{6}}{k_{6} + k_{7} + k_{14}}\right) \left(\frac{k_{11}}{k_{10} + k_{11} + k_{12}[\text{M}]}\right)\right] + \gamma\left(\frac{k_{12}[\text{M}]}{k_{10} + k_{11} + k_{12}[\text{M}]}\right) \left(\frac{k_{6}}{k_{6} + k_{7} + k_{14}}\right) (\text{II})$$

$$Y(\text{Si}_{3}\text{H}_{8}) = \left[\frac{k_{8}}{k_{8} + k_{9}[\text{M}]}\right] \left[(f_{\text{A}} + f_{\text{C}}) + \gamma\left(\frac{k_{7}}{k_{6} + k_{7} + k_{14}}\right) + \gamma\left(\frac{k_{6}}{k_{6} + k_{7} + k_{14}}\right) \left(\frac{k_{11}}{k_{10} + k_{11} + k_{12}[\text{M}]}\right)\right] + \gamma\left(\frac{k_{6}}{k_{6} + k_{7} + k_{14}}\right) \left(\frac{k_{10}}{k_{10} + k_{11} + k_{12}[\text{M}]}\right) (\text{III})$$

$$Y(\text{H}_{2}) = (f_{4} + f_{8} + 2f_{\text{C}} + f_{7} + f_{8}) + \frac{1}{2}$$

$$\begin{bmatrix} \frac{k_{8}}{k_{8} + k_{9}[M]} \end{bmatrix} \begin{bmatrix} (f_{A} + f_{C}) + \gamma \left(\frac{k_{7}}{k_{6} + k_{7} + k_{14}}\right) + \\ \gamma \left(\frac{k_{6}}{k_{6} + k_{7} + k_{14}}\right) \left(\frac{k_{11}}{k_{10} + k_{11} + k_{12}[M]}\right) \end{bmatrix} + \\ \gamma \left(\frac{k_{6}}{k_{6} + k_{7} + k_{14}}\right) \left(\frac{k_{10}}{k_{10} + k_{11} + k_{12}[M]}\right) + 3k_{14}[SiH_{3}]^{2}$$
(IV)

$$Y(\text{solid}) = \gamma \left( \frac{k_{14}}{k_6 + k_7 + k_{14}} \right)$$
 (V)

Negative terms in (I) representing SiH<sub>4</sub> formation via reactions

7 and 11 do not appear because although SiH<sub>4</sub> is made, so is SiH<sub>2</sub> which rapidly inserts into SiH<sub>4</sub> with the net result that there is no change in the value of  $Y(-SiH_4)$ . Inserting (III) into (I) and bearing in mind that  $f_A + f_B + f_C + f_D + f_E = 1$ , we obtain

$$Y(-SiH_4) = 2(1 + f_C) + Y(Si_3H_8)$$
 (VI)

and inserting (I) into (IV) and redefining  $k_{14}[SiH_3]^2$  as Y(solid), we obtain

$$Y(H_2) = Y(-SiH_4) - (1 + f_C) + 3Y(solid)$$
 (VII)

While the actual values of Y(x) could not be measured, the values for  $f_x$  were measured. Hence, we can rewrite (VI) as

$$\frac{2(1+f_{\rm C})}{Y(-{\rm SiH_4})} + f({\rm Si_3H_8}) = 1$$
(VIII)

which leads to the following values for Y(x):

$$Y(\text{SiH}_4) = 2.06(1 + f_C)$$
  

$$Y(\text{Si}_2\text{H}_6) = 0.80(1 + f_C)$$
  

$$Y(\text{Si}_3\text{H}_8) = 0.06(1 + f_C)$$
  

$$Y(\text{H}_2) = 1.42(1 + f_C)$$
  

$$Y(\text{Si}_2(\text{S})) = 0.13(1 + f_C)$$

Appropriate substitution into (VII) gives a theoretical value for  $Y(H_2)$  of  $1.45(1 + f_C)$ . If we bear in mind that some H incorporation into the solid material occurs, this is quite good agreement. Since  $f_C$  is less than about 0.1, vide ante, the primary yield for the loss of silane is approximately 2.1 molecules per electron. Using this value for  $Y(-SiH_4)$  and the measured values of  $R(-SiH_4)$ , we find that the multiplication factor, m, is in the range 20–35. This is in reasonable agreement with the estimate that 10–20 electron–ion pairs are produced for each primary electron in order to sustain a glow discharge.

A further simplification can be introduced. Since the activation energy for the creation of  $Si_2H_6^*$  is only 1.3 kcal/mol,<sup>17</sup> it is reasonable to assume that collisional stabilization of  $Si_2H_6^*$  will occur upon 1–2 collisions, hence  $k_9[M] > k_8$ . Thus the first term in (II) is approximately 1 and the first term in (III) is very small. This leads to the following simplified expressions for the rate equations for the higher silane products:

$$Y(\text{Si}_{2}\text{H}_{6}) = (f_{\text{A}} + f_{\text{C}}) + \gamma \left(\frac{k_{7}}{k_{6} + k_{7} + k_{14}}\right) + \gamma \left(\frac{k_{7}}{k_{6} + k_{7} + k_{14}}\right) \left(\frac{k_{11} + k_{12}[\text{M}]}{k_{10} + k_{11} + k_{12}[\text{M}]}\right) (\text{IX})$$

$$Y(Si_{3}H_{8}) = \gamma \left(\frac{k_{6}}{k_{6} + k_{7} + k_{4}}\right) \left(\frac{k_{10}}{k_{10} + k_{11} + k_{12}[M]}\right) \quad (X)$$

It can be seen from these expressions that

$$Y(Si_2H_6) + Y(Si_3H_8) + Y(solid) = 1$$
 (XI)

which is actually a statement of the Si-atom balance.

Substitution of the measured values of Y(solid) into (V) and using the approximation that  $\gamma = 0.91$  gives a value for  $k_{14}/(k_6 + k_7 + k_{14})$  of 0.14, hence  $(k_6 + k_7)/(k_6 + k_7 + k_{14})$  is 0.86. Thus,  $k_{14}/(k_6 + k_7)$  is 0.16, indicating that about 16% of the SiH<sub>3</sub> generated is going into film formation. The reported value for  $k_7/k_6$  is 0.70.<sup>21</sup> Substituting this value into (X), along with the measured values of  $Y(\text{Si}_3\text{H}_8)$  and the approximate value of  $\gamma$  and the calculated value of  $k_6/(k_6 + k_7 + k_{14})$ , yields a value of 0.07 for  $k_{10}/(k_{10} + k_{11} + k_{12}[\text{M}])$ , hence  $(k_{11} + k_{12}[\text{M}])/(k_{10} + k_{11} + k_{12}[\text{M}])$  is 0.93. These results are quite different from those obtained for the UV photolysis, wherein the respective ratios are 0.78 and 0.12 for SiH<sub>4</sub> at 2.1 torr. However, our results are consistent with the experimental observations in that if  $k_{10}$  were

<sup>(21)</sup> B. Reimann, A. Matthen, R. Lampert, and P. Potzinger, Ber. Bunsenges. Phys. Chem., 81, 500 (1977).

larger than  $k_{11} + k_{12}[M]$ ,  $(k_{11} + k_{12}[M])/(k_{10} + k_{11} + k_{12}[M]) \approx k_{11} + k_{12}[M]$ , and the value of  $Y(\text{Si}_2\text{H}_6)$  as given by (IX) would show a pressure dependence, which we do not observe. We cannot determine the extent of the disproportionation reaction 7 from the results of this study. In the case that  $2\text{SiH}_3$  reacts to give  $\text{SiH}_2 + \text{SiH}_4$  which then forms  $\text{Si}_2\text{H}_6$  and/or solid, these stable products would still be scavengeable by NO. This does not,

however, detract from the importance of  $SiH_3$  in the plasma process, which is the conclusion of this study.

Acknowledgment. We thank A. Catalano for his critical and timely discussions during the course of the study.

**Registry No.** SiH<sub>4</sub>, 7803-62-5; Si<sub>2</sub>H<sub>6</sub>, 1590-87-0; Si<sub>3</sub>H<sub>8</sub>, 7783-26-8; NO, 10102-43-9.

# Time-Resolved Fluorescence-Detected Magnetic Resonance and Fluorescence Studies of Trialkylamines Irradiated by Pulse Radiolysis in Alkane Solvents

## Steven M. Lefkowitz and Alexander D. Trifunac\*

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 (Received: April 15, 1983; In Final Form: May 17, 1983)

Time-resolved fluorescence-detected magnetic resonance (FDMR) studies of irradiated alkane solutions of trialkylamines and scintillators reveal the EPR spectra of the trialkylaminium radicals, formed by scavenging solvent radical cations. A qualitative kinetic analysis indicates that the growth of the triethylaminium radical (TEA<sup>+</sup>) FDMR signal occurs on similar time scales in both *n*-hexane and cyclohexane, suggesting that, in cyclohexane, TEA<sup>+</sup> is formed by scavenging the lower mobility, "trapped" cyclohexane radical cations. Fluorescence results indicate that TEA quenches both scintillator fluorescence and total FDMR intensities to a greater extent than is expected from amine scavenging of solvent holes. TEA also exhibits an intense, relatively long-lived fluorescence which is apparently not produced by radical ion recombination or energy transfer.

#### Introduction

Aliphatic amines, by virtue of their low ionization potentials, have been widely used as reducing agents in photochemistry and radiation chemistry, and triethylamine (TEA) may be considered paradigmatic in this respect. In the radiolysis of an alkane solvent (R), the initial ionizing event results in the formation of solvent radical cations (holes) and electrons, e.g.

$$R \xrightarrow{} R^+ + e^- \tag{1}$$

TEA can then efficiently react with the solvent hole to form (presumably) the triethylaminium radical

$$R^+ \cdot + TEA \to R + TEA^+ \cdot$$
 (2)

An aromatic scintillator, such as 2,5-diphenyloxazole (PPO), can efficiently scavenge electrons to yield the radical anion

$$PPO + e^- \to PPO^-. \tag{3}$$

The high electron mobility seen in these solvents results in electron scavenging rate constants ca. 100 times those of positive charge scavenging, and with the time resolution and scintillator concentrations relevant to this work, we may consider the electrons to be completely reacted. PPO is also an efficient hole scavenger, reacting to form  $PPO^+$ .

The recombination events which may give rise to scintillator fluorescence, presupposing the electron transfer is sufficiently exothermic to pump a scintillator excited state, are as follows:

$$R^+ \cdot + PPO^- \cdot \to R + PPO^*$$
 (4)

 $TEA^+ + PPO^- \to TEA + PPO^*$  (5)

$$PPO^{+} + PPO^{-} \rightarrow PPO + PPO^{*}$$
(6)

By adjusting the concentrations of the amine and scintillator, the relative contribution of each recombination event to the overall **PPO** fluorescence yield may be varied.

We have previously demonstrated that the EPR spectrum of a geminate radical ion pair, recombining to yield a fluorescent species, may be derived by time-resolved fluorescence-detected magnetic resonance (FDMR).<sup>1</sup> This technique has revealed the EPR spectra of the short-lived radical cations of *n*-hexane and cyclohexane, from the modulation of fluorescence from recombination (4), at low scintillator concentrations.<sup>2</sup> The EPR spectrum of the cyclohexane radical cation exhibited resolved hyperfine splittings of less than 10 G, indicating the presence of a physically "trapped" cyclohexane hole, which apparently coexists with the high mobility hole species noted in conductivity studies.<sup>3</sup>

In the present study, the FDMR spectra of a series of aliphatic amines have been observed, originating in the fluorescence from recombination (5), in an alkane solution of the amine and scintillator. These have been assigned as the EPR spectra of the appropriate aminium radicals. The triethylaminium radical exhibits a well-resolved FDMR spectrum, which has allowed the qualitative time resolution of the solvent hole scavenging by TEA. While in *n*-hexane, the growth of the TEA<sup>+</sup> spectrum follows the time dependence expected for a diffusion-controlled scavenging rate, cyclohexane solutions surprisingly show a similar time dependence, suggesting that the highly mobile cyclohexane hole is not efficiency scavenged by the amine to form TEA<sup>+</sup>. We also report preliminary results indicating an unusual quenching of PPO fluorescence by TEA, and an unexpectedly high yield of long-lived TEA fluorescence emission in these systems.

## **Experimental Section**

The FDMR experiments, consisting of a pulsed 3-MeV electron Van de Graaff ionizing source, a pulsed X-band microwave source, a boxcar integrator to view the fluorescence, and a field-swept magnet, have been previously described.<sup>1</sup> An electron beam pulse of 5-ns duration and ca. 30-mA peak current, pulsed at 400 Hz, was used. Fluorescence of PPO was viewed at 355 nm, and anthracene- $d_{10}$  at 390 nm, with a bandpass of ca. 15 nm. A stepper motor has been added to the monochromator to allow the recording of dispersed fluorescence spectra at selected viewing times after excitation. In FDMR and fluorescence descriptions, we take t

<sup>(1)</sup> Smith, J. P.; Trifunac, A. D. J. Phys. Chem. 1981, 85, 1645.

<sup>(2)</sup> Smith, J. P.; Lefkowitz, S. M.; Trifunac, A. D. J. Phys. Chem. 1982, 86, 4347.

<sup>(3)</sup> Warman, J. M. In "The Study of Fast Processes and Transient Species by Electron Radiolysis"; Busi, G.; Baxendale, J. H. E.; Reidel: Boston, 1982.