Kinetics of Silane Decomposition by Atomic and Molecular Nitrogen Metastables

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We have studied the reactions of a number of metastable nitrogen species with silane in a discharge-flow reactor. By monitoring the decays in the metastable number densities both as a function of time and as a function of silane number density, we have determined reaction rate coefficients, in units of 10 \(^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), for the following species: \(N_2(A^2Σ^+u'=0,1)\), \(N(2D)\), \(N(2P)\). In addition, we have estimated an upper limit to the rate coefficient for the reaction between \(N(2S)\) atoms upstream from the silane addition inlet enhances the number densities of \(N(2P)\) and \(N(2D)\) in the flow and, in addition, the previously observed UV emissions. The UV spectral features are further enhanced when silane is added to the orange afterglow of active nitrogen, which is a mix of all the metastables studied and, in addition, vibrationally excited, ground-electronic-state nitrogen. We suggest that the decomposition of silane is initiated by absorbing several quanta from vibrationally excited nitrogen, followed by H atom stripping in reactions of SiH\(_4\) and its fragments with N atoms. The observed excitations result from energy-transfer reactions between the various nitrogen metastables and the silane fragments in the flow.

Introduction

Silicon nitride films, which are important in various semiconductor applications, can be generated by plasma vapor deposition processes. Typical plasmas are created by either microwave or radio-frequency discharges through mixtures of silane and nitrogen. Developing models of such plasmas, so that the plasma deposition process can be better understood, requires a knowledge of the kinetics of various nitrogen species with silane and its fragments. Such kinetic information is sparse.

Horie et al.\(^1\) reported chemiluminescence from various spectral features when silane was added to active nitrogen in a discharge-flow reactor. In addition, they monitored decay profiles of atomic nitrogen and silane. However, they made no quantitative estimates of kinetic rates.

We have measured the rate coefficients for the interactions of silane with a number of nitrogen species quantitatively. These studies include the atomic and molecular metastables \(N_2(A^2Σ^+u'=0,1)\), \(N(2D)\), and \(N(2P)\). In addition, we have estimated an upper limit to the rate coefficient for the reaction between \(N(2S)\) and silane. We have also observed chemiluminescent emissions from mixtures of silane with active nitrogen that was produced under several different sets of conditions. These observations permit us to speculate on the mechanisms of silane decomposition in active nitrogen.

Experimental Section

These experiments were all done in the 2-in.-diameter discharge-flow reactor that we have described in detail previously.\(^2\) The nitrogen species were generated by various discharge techniques at the upstream end of the reactor and detected further downstream. We have documented our procedures for generating these techniques and documents the relevant publications. Table I summarizes these techniques and documents the relevant publications. Three of these species, \(N_2(A^2Σ^+u'=0,1)\), \(N(2D)\), and \(N(2S)\), are formed inside a discharge. The other two species, \(N_2(A)\) and \(N(2P)\), are generated by energy-transfer processes. The precursor species for these two metastables are consumed completely in the upstream portion of the flow reactor, above the silane injector. In all cases, conditions downstream from the silane injector are such that additional production mechanisms for all species studied are insignificant. Table I also lists the range of experimental conditions under which we studied each metastable.

The silane was added to the reactor through a movable injector. The rate coefficients were determined by monitoring the decay of the nitrogen species as a function of silane number density and of reaction time.

Chemiluminescent emissions were observed by recording spectra between 200 and 850 nm under the different sets of operating conditions. We used a 0.5-m scanning monochromator that was equipped with a thermoelectrically cooled photomultiplier and a photon-counting rate meter. A computer-based, data acquisition system digitized the output of the photon counter and stored the data for subsequent analysis.

The variation in the response of the monochromator as a function of wavelength was determined by scanning the output of standard quartz-halogen and deuterium lamps. A BaSO\(_4\) screen reflected the lamp emission into the monochromator, thereby ensuring that the optics were filled. Calibrations obtained from the two lamps agreed excellently in the region of spectral overlap, 300–400 nm.

Results

Kinetic Measurements. The rate of change of the nitrogen species, \(N_x^*\), as a function of reaction time is

\[
\frac{d[N_x^*]}{dt} = -k_{\text{wall}} + k_{\text{rad}}[\text{SiH}_4][N_x^*]
\]

where \(k_{\text{wall}}\) is the effective first-order rate of diffusion to the reactor walls. The reactor walls quench the metastables with near unit efficiency.\(^6\) Other species in the reactor such as \(N_2\) and Ar are not significant quenchers under the conditions employed. In all instances, the number density of added silane is much greater than that of the various nitrogen metastables. Removal of the metastables by silane, therefore, is effectively first order, and eq 1 can be solved to give

\[
\ln \left(\frac{[N_x^*]}{[N_x^*]_0}\right) = -k_{\text{wall}} + k_{\text{rad}}[\text{SiH}_4]t
\]

where the subscript 0 implies the number density prior to SiH\(_4\) addition.

In flow-reactor studies of this type the effective reaction time is given by 0.62 times the ratio of the distance between the injector and the detection region, \(z\), to the bulk flow velocity of the gas, \(v\). The factor of 0.62 corrects for fluid mechanical effects.\(^9\)

*\(k_{\text{rad}}\) is the effective first-order rate of diffusion to the reactor walls.

**\(k_{\text{rad}}\) is the effective first-order rate of diffusion to the reactor walls.


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The intercept in Figure 2 shows that removal by silane as a function of reaction time for five different coefficient, \( r \), at constant flow velocity and total pressure then, will give the desired rate coefficient. This procedure also corrects for imperfect mixing at the injector.

![Figure 1](image)

**Figure 1.** Decay of \( N_2(A, \omega=0) \) as a function of SiH4 number density at three different reaction times.

In practice, we fix the reaction distance and measure the decay coefficient, \( \Gamma \), at constant flow velocity and total pressure

\[
\Gamma = -\frac{1}{d[N_2^*]} \frac{d[N_2^*]}{d[SiH_4]} = 0.62 k_{reac}/\theta (3)
\]

The slope of a plot of \( \Gamma \) as a function of reaction time, 0.62\( z/\theta \), then, will give the desired rate coefficient. This procedure also corrects for imperfect mixing at the injector.

Figure 1 shows the decay of \( N_2(A, \omega=0) \) as a function of silane number density at three different reaction times. The slopes of the three lines are decay coefficients at the different reaction times.

Figure 2 shows a plot of the decay coefficients for \( N_2(A, \omega=0) \) removal by silane as a function of reaction time for five different reaction times. The slope of this line is the rate coefficient for \( N_2(A) \) quenching by SiH4. The intercept in Figure 2 shows that reagents, under the conditions employed, take approximately 1.5 ms to mix. The effective mixing time is a function of flow velocity, pressure, and injector design. It must be determined for each set of experimental conditions.

Table II summarizes all of the rate coefficient measurements. The error limits include the statistical errors in the data analysis as well as estimated systematic uncertainties resulting from such things as errors in calibrations of flow meters, pressure transducers, reproducibility, etc.

**Chemiluminescence Observations.** Spectra were measured under four sets of conditions: (1) in the afterglow containing only \( N_2(A) \), (2) in the presence of recombing N atoms, (3) in the presence of recombing N atoms to which \( N_2(A) \) has been added and fully consumed upstream from the silane injector, and (4) in the short-lived, orange afterglow generated by a microwave discharge through a mixture of \( N_2 \) dilute in argon. The recombing N atom afterglow is produced by passing the effluents of discharged \( N_2/Ar \) mixtures through a glass wool plug. This procedure deactivates any nitrogen metastables produced in the discharge and generally deactivates vibrationally excited, ground-state nitrogen.11 After finishing these studies, however, we performed some Penning ionization experiments12 on this afterglow and discovered the vibrational deactivation to be incomplete. About a third of the molecular nitrogen was vibrationally excited with about 12% of the \( N_2(X, \omega=0) \) in vibrational levels five and above. The role of \( N_2(X, \omega) \) in the silane fragmentation

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**Table I: Metastable Nitrogen Production Techniques**

<table>
<thead>
<tr>
<th>species</th>
<th>excitation energy, eV</th>
<th>production</th>
<th>detection</th>
<th>([N^<em>]_0 ) or ([N_2^</em>]_0 ) particles cm(^{-3})</th>
<th>([\text{SiH}<em>4]</em>{\text{max}} ) molecules cm(^{-3})</th>
<th>range of mixing times, ( \text{ms} )</th>
<th>bulk flow velocity, cm s(^{-1})</th>
<th>press., Torr</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2(A_1^2\Sigma_u^+) )</td>
<td>6.17</td>
<td>( \text{Ar}^* + N_2 \rightarrow N_2^* + \text{Ar}; \text{Ar}^* ) produced in dc discharge ( d_c )</td>
<td>( N_2(A-X) ) emission (220-350 nm)</td>
<td>( 4 \times 10^9 ) (( \alpha' = 0 ))</td>
<td>( 4 \times 10^{13} )</td>
<td>10-18</td>
<td>1500</td>
<td>2.0</td>
<td>2</td>
</tr>
<tr>
<td>( N_2(a'^2\Delta \Sigma_u^-) )</td>
<td>8.3</td>
<td>( N_2(a'^2\Delta \Sigma_u^-) ) emission (140-180 nm)</td>
<td></td>
<td>( \approx 10^9 )</td>
<td></td>
<td>1 ( \times 10^{13} )</td>
<td>2-4.5</td>
<td>3200</td>
<td>1.5</td>
</tr>
<tr>
<td>( N(D) )</td>
<td>2.38</td>
<td>( N_2(A-X) ) emission (140-180 nm)</td>
<td>vacuum-UV resonance fluorescence</td>
<td>( 4 \times 10^{10} )</td>
<td></td>
<td>2 ( \times 10^{13} )</td>
<td>3-8</td>
<td>3200</td>
<td>1.5</td>
</tr>
<tr>
<td>( N(P) )</td>
<td>3.58</td>
<td>( N_2(A) + N_2^{(S)} \rightarrow N_2(P) + N_2(X) )</td>
<td>( N_2(P-S) ) emission at 347 nm</td>
<td>( 1 \times 10^9 )</td>
<td></td>
<td>5 ( \times 10^{13} )</td>
<td>9-16</td>
<td>1650</td>
<td>1.8</td>
</tr>
<tr>
<td>( N(S) )</td>
<td>( \text{Silane decomposition} )</td>
<td>( \text{Silane decomposition} )</td>
<td>( N_2(B-A) )</td>
<td>( 8 \times 10^{12} )</td>
<td></td>
<td>3 ( \times 10^{13} )</td>
<td>16</td>
<td></td>
<td>1650</td>
</tr>
</tbody>
</table>

*Effective reaction time = 0.62\( z/\theta \).*

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**Table II: Rate Coefficients for Metastable Nitrogen Reactions with Silane**

<table>
<thead>
<tr>
<th>nitrogen species</th>
<th>rate coefficient, ( 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} )</th>
<th>( \text{SiH}_4 ) range, Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2(A_1^2\Sigma_u^+, \omega=0) )</td>
<td>0.84 ( \pm 0.16 )</td>
<td>1-10</td>
</tr>
<tr>
<td>( N_2(A_1^2\Sigma_u^+, \omega=1) )</td>
<td>1.12 ( \pm 0.24 )</td>
<td>1-10</td>
</tr>
<tr>
<td>( N_2(a'^2\Delta \Sigma_u^-, \omega=0) )</td>
<td>20.7 ( \pm 5.0 )</td>
<td>1-10</td>
</tr>
<tr>
<td>( N(D) )</td>
<td>5.7 ( \pm 1.3 )</td>
<td>1-10</td>
</tr>
<tr>
<td>( N(P) )</td>
<td>0.09 ( \pm 0.03 )</td>
<td>1-10</td>
</tr>
<tr>
<td>( N(S) )</td>
<td>(&lt;0.008 )</td>
<td>1-10</td>
</tr>
</tbody>
</table>

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counted and indeed seems likely.

of the silane.

course, of the N2(A3Π, ‾X1Σg+), Vegard-Kaplan, bands. Figure

bands was characteristic of that generated by N atom recombi-

Figure 4.

Figure 4. Spectrum from adding SiH₄ to active nitrogen.

processes observed in this afterglow, therefore, cannot be dis-

No spectral features were observed between 200 and 850 nm

silane was added directly to N2(A) with the exception, of

3 shows the UV spectra generated under conditions 2 and 3, given

above, while Figure 4 shows the UV spectrum excited under

all three sets of conditions result in essentially similar

spectral features related to SiH₄ addition except that the intensities

increase substantially from condition 2 to 4. Major emissions

include a number of lines of atomic silicon, an apparent continuum

emission between 250 and 450 nm, and the A-X bands of SiH, SiN, and NH. All three spectra imply substantial decomposition of the silane.

The spectra in the 500-850-nm region for conditions 2 and 4

consisted primarily of the nitrogen first-positive bands, N₂-

(BΠ₁/₂-A¹Σ⁺), with an apparent underlying continuum when

silane was introduced into the reactor. No spectrum was taken

for condition 3, since it should be similar to that of condition 2.

For condition 2, the vibrational distribution of the first-positive

bands was characteristic of that generated by N atom recombi-

nation,13 while that for condition 4 is characteristic of the excitation of N₂(BΠ₂) generated in the energy-transfer reaction between

N₂(A¹Σ⁺) and N₂(X₂Σ⁺).14

The position of silane injection for condition 3, the addition of

N₂(A) to recombining N atoms, was somewhat downstream

from the point at which the N atoms had quenched all of the N₂(A).

Thus, the major difference between condition 3 compared to

condition 2 should be the presence of N(²P,³D) metastables in

the flow.3 The presence of N(²P) under condition 3 is evident

in Figure 3 by the N(²P-⁺S) emission line at 347 nm. While

N(²P) is also a constituent of the flow under condition 4, the

347-nm line is too weak to register on the scale of Figure 4. Some small enhancement to the number density of vibrationally excited,

ground-state molecular nitrogen is also likely under condition 3

compared to condition 2 because the energy-transfer reaction

between N₂(A) and N(²S) to make N(²P) is exoergic by 2.6 eV.

This excess energy is likely to be retained as internal energy in

N₂(X).

Discussion

Table II shows that the rate coefficients for quenching N₂(A),

N₂(a⁠), and N(²D) are all tenth gas kinetic or faster. The most

probable result of the quenching of N₂(A) and N₂(a⁠) by silane

will be SiH₄ fragmentation. Both molecular metastables contain

enough energy to fragment the silane into either SiH₃ and H or

SiH₂ and H₂ (see Table III). The atomic metastable N(²D) can

only react with silane to give SiH₃ and NH as the products. Our

results show it must do this quite efficiently unless the quenching

mechanism is just E-V transfer to vibrational modes of SiH₄. The

higher energy atomic metastable, N(²P), reacts some 2 orders of

magnitude more slowly in spite of having a reactive channel similar

to that for N(²D) and, in addition, a possible quenching channel

that results in the generation of SiH₃ and H₂. Ground-state

nitrogen atoms have no exoergic channel for reacting with silane,

in accord with our failure to observe any signs of N(²S) removal

when silane was added to the reactor.

The energetics of silane decomposition by nitrogen metastables

are such that no simple elementary reaction can be responsible

for the observed fragment excitation.15-17 What must be hap-

pening instead is that the constituents in the active nitrogen de-

compose the silane, and the resultant fragments are then excited

in subsequent energy-transfer reactions. Table III lists a number

of likely first steps in the silane decomposition along with the

associated exoergicities of the decomposition reactions. Since

ground-state atomic nitrogen does not react with silane, some other

species in the recombining-nitrogen afterglow must be responsible

for the first step in the decomposition. One possibility for these

other species would be the N₂(a⁠) and N₂(X₂) which are generated

in the homogeneous recombination of the N atoms in the after-

glow. Given that the N atom number density in the afterglow

was only 8 x 10⁵ atoms cm⁻³, the steady-state number densities

d of these species will be quite small, ≤10⁶ molecules cm⁻³. Silane

decomposition by these species, therefore, should be minimal.

More likely is fragmentation by vibrationally excited N₂(X₂) that

was produced in the discharge. Our Penning ionization observation18

indicated a likely number density of N₂(X₂=25) in excess of 10¹⁴

molecules cm⁻³. The role of N₂(X₂=25) can flow two pathways. Both cases involve transferring vibrational energy from the N₂(X₂=25) to SiH₄. Such an energy-transfer process should be highly probable given that one-quantum transfer from


The decomposition of silane on the order of a milliTorr, each silane molecule will undergo composition can occur rapidly even at the modest N(4S) number densities of the present experiments. If these reactions are moderately fast, this further decomposition can occur rapidly even at the modest N(4S) number densities of the present experiments (~10^13 atoms cm^-3). The final decomposition step, that between SiH and N('S), is endoergic if the nitrogen atoms are electronically excited. Atomic and molecular metastable nitrogen, N(2D), N2(A), and N2(a'), react rapidly with silane, leading to SiH4 fragmentation. In addition, silane appears to be decomposed efficiently by vibrationally excited, ground-electronic-state molecular nitrogen. This latter fragmentation most probably occurs when N(4S) strips H atoms from silane molecules that have absorbed two or more N2(X,u') quanta. Also possible would be silane dissociation by N2(X,u') either in one step with many quanta (on the order of 10) transferred to the SiH4 or by a series of successive transfers a few quanta at a time.

**Summary**

Atomic and molecular metastable nitrogen, N(2D), N2(A), and N2(a'), react rapidly with silane, leading to SiH4 fragmentation. In addition, silane appears to be decomposed efficiently by vibrationally excited, ground-electronic-state molecular nitrogen. This latter fragmentation most probably occurs when N(4S) strips H atoms from silane molecules that have absorbed two or more N2(X,u') quanta. Also possible would be silane dissociation by N2(X,u') either in one step with many quanta (on the order of 10) transferred to the SiH4 or by a series of successive transfers a few quanta at a time.

**Acknowledgment.** We appreciate support for this work from PSI under internal research funds. We also acknowledge helpful discussions and correspondence with Peter Haaland on silane thermochemistry.

New Features of Stirring Sensitivities of the Belousov-Zhabotinskii Reaction

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The sensitivity to stirring shown by the oscillatory Belousov-Zhabotinskii (BZ) reaction when carried out in batch mode has been experimentally examined. Different series of experiments were designed in order to test the influence of both the flow rate of a deaerating agent and the reactant initial concentrations on the observed stirring susceptibility. In addition, distinctive stirring effects associated with the different phases of the oscillatory reaction were analyzed. The experimental results indicate that stirring effects strongly depend on the initial concentrations of the BZ mixture and on the detailed chemical dynamics inherent in each phase of the reaction.

I. Introduction

Chemical instabilities, as paradigms of nonlinear effects corresponding to dynamics operating far from equilibrium regimes, have been mostly described in past years in terms of homogeneous models, avoiding any reference to heterogeneities. Yet it is presently well-documented that effects originated in nonideal mixing conditions not only exist under the usual operating modes of real experiments but may also exert noticeable influences enhancing, suppressing, or modifying normal patterns of behavior such as temporal oscillations or multistability. Even recently, features of irreproducibility likely mediated by stirring, which have been observed in certain chemical systems, have motivated preliminary experimental1 and theoretical studies.3 Commonly, stirring effects within the context of oscillatory or multistable chemical dynamics have attracted the attention of both theoreticians2 and experimentalists,6,12-22 The existing literature refers

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