CHEMIIONIZATION AND CHEMILUMINESCENCE IN THE REACTION OF SiH₄ WITH ACTIVE NITROGEN

O. HORIE¹, P. POTZINGER and B. REIMANN

Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a.d. Ruhr, West Germany

Received 4 June 1986

The reaction of SiH₄ with active nitrogen in a discharge-flow system was found to produce strong chemiionization besides the well-known SiN^{*} and Si^{*} chemiluminescences. In the presence of a large initial excess of N atoms, both N and SiH₄ disappeared completely in the course of the reaction. Addition of as little O₂ as 10^{13} cm⁻³ was sufficient to quench the chemiluminescence and suppress chemiionization completely. A mechanism explaining the experimental findings has to include a slow initiation step followed by a branched chain.

1. Introduction

The reaction of active nitrogen with compounds containing silicon atoms is known to produce chemiluminescence from electronically excited SiN* radicals [1-3]. Despite the wealth of spectroscopic data [4,5] no attention has been paid to the kinetics, mechanism, and reaction products. More recently the system has been studied by a Czechoslovak group, principally from the point of view of plasma-assisted silicon nitride deposition [6].

During the course of a study on the reaction of SiH_4 with O atoms [7], it became necessary to examine the effect of the reaction N + SiH_4 on the kinetic measurement, since O atoms were generated in the titration reaction N + NO \rightarrow N₂ + O. We have found that the system SiH_4 + active nitrogen produces strong chemiionization associated with chemiluminescence, and that both the SiH_4 and N atom concentrations show interesting decay profiles. We report the results of these observations and present a preliminary discussion of the reaction mechanism.

0 009-2614/86/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Divison)

2. Experimental

A discharge-flow system coupled to a mass-spectroscopic detection system [8] with several modifications was used in this study. The side arm of the previous reactor (reactor C in fig. 1 of ref. [8]) which had served as the microwave discharge tube was replaced by a 50 cm long flow tube made of Pyrex glass having the same inside diameter (26 mm) as that of the reactor. A movable injector and a microwave discharge tube were attached to the flow tube. In short, the observation system consisted of two similar discharge-flow reactors in tandem connected at right angles. A four-way array of ports was provided at right angles to the flow tube near the entrance to the second reactor.

The chemiluminescence was observed through one of the two quartz windows attached to the two opposing ports. The emitted light was chopped at 405 Hz, collected using a quartz lens (f = 3.0) and focused onto the entrance slit of a 25 cm Schoeffel monochromator (GM 250, f = 3.6) equipped with a 1180 lines mm⁻¹ grating blazed at 240 nm. The signal was detected by a cooled Hamamatsu R 955 photomultiplier, whose output was fed into a PAR 124A lock-in amplifier. Chemiionization was observed by applying 160 V dc across two 25 mm diameter, stainless-steel disc electrodes attached to the two opposing ports.

¹ Present address: Max-Planck-Institut für Chemie, D-6500 Mainz, West Germany.

The electrodes were 40 mm apart. The chemiion current was measured as a dc potential across a 1 M Ω resistance with a Fluke (8800A) digital multimeter.

The same gas-handling procedure was used as in ref. [8]. Nitrogen atoms were generated in a microwave discharge through a N₂/He mixture in the side arm. The N atom concentration was measured by means of the titration reaction N + NO \rightarrow N₂ + O. The end-point of the titration was determined either by observing visually the extinction of the NO^{*}₂ air-afterglow emission, or by measuring the chemiion current due to NO⁺ [9,10]. Occasionally the mass-spectroscopic method [8] was also used. The three methods always gave results which agreed within 10%.

Helium (99.996%), oxygen (99.995%), nitrogen $(\geq 99.99\%)$, SiH₄ (99.9%) and SiD₄ (99% isotopic purity) were used without further purification. NO was purified by passing it through Ascarite (Fluka) several times.

All measurements were carried out at room temperature (298 ± 2 K) and at a pressure of about 400 Pa. The average linear flow rate in the flow tube was between 500 and 1000 cm s⁻¹. N atom concentrations ranged from 0.7 to 2.8 × 10¹⁴ cm⁻³, those of SiH₄ from 0.2 to 2.5 × 10¹³ cm⁻³. The ratio of their initial concentrations, $m = [N]_0/[SiH_4]_0$ varied between 9 and 175.

3. Results and discussion

3.1. Chemiluminescence and chemiionization

When SiH₄ was introduced into a flow containing active nitrogen $(N/N_2^* - hereafter this notation will$ be used when appropriate), the orange N₂^{*} first positive emission disappeared and a blue-violet emissioncharacteristic of the SiN* chemiluminescence ap $peared. Under the conditions of <math>30 \le m \le 70$, the blue-violet emission was preceded by a bright luminescence having a milky-pink color. At other concentration ratios the emission appeared as a single milky luminescence.

Two SiN* transitions, the very strong $B^{2}\Sigma^{+} \rightarrow X^{2}\Sigma^{+}$ and the much weaker $D^{2}\Pi \rightarrow A^{2}\Pi$, were observed in the chemiluminescence. The other two known transitions, $K^{2}\Sigma \rightarrow A^{2}\Pi$ and $L^{2}\Pi \rightarrow A^{2}\Pi$ [5] were not unequivocally identified due to low intensities. Also, several emission lines due to Si atoms were observed at 221 nm (${}^{3}P-{}^{3}D$), 243 nm (${}^{1}D-{}^{1}D$), 251 nm (${}^{3}P-{}^{3}P$), 263 nm (${}^{1}S-{}^{1}P$), 288 nm (${}^{1}D-{}^{1}P$), 299 nm (${}^{1}D-{}^{3}P$), and 301 and 302 nm (${}^{3}P-{}^{5}S$) [11]. No emissions due to electronically excited SiH, Si₂, NH, or NH₂ radicals were detected.

In addition, a "continuum" emission extending from about 450 nm to or beyond 810 nm was observed mainly in the milky-pink region (fig. 1). It is possible that the continuum consists of unresolved, closely packed overlapping bands. Depending on the distance between the observation port and the probe end, Z, and the ratio m, some bands of the N₂ first positive emission as well as some SiN* transitions were detectable in the continuum. It is inferred from fig. 1b that at least two emitters are responsible for the continuum, one emitting between 450 and 687 nm and the other starting at 687 nm and extending beyond 800 nm, although they were not identified in this study. It should be noted that two peaks marked w, w' and y in fig. 1 may not belong to the N₂^{*}-first positive system. If they do, it may imply that they are enhanced by some energy-transfer processes.

An interesting finding of this study is the chemiionization. The ion current observed in the $SiH_4 + N/N_2^*$ system was comparable to that due to NO⁺ in the NO + N/N₂* system [10]. It must be pointed out, however, that the ionization in the present study was observed in the absence of O atoms. It is different from the enhancement of the chemiion current which is caused by the addition of C_2F_4 or other compounds to the system NO + N/N₂* [21]. An attempt was made to identify the ionic species mass-spectrometrically using the original reactor. However, it was not possible to detect anything, probably due to the sampling skimmer construction which was not designed for chemiion detection, i.e. a stainless-steel skimmer, the presence of a chopper, etc.

3.2. The dependence of the chemiluminescence intensities and the chemilon current on $[N]_0$ and $[SiH_4]_0$

The dependence of the chemiluminescence intensities and the chemilon current on Z was measured for various $[SiH_4]_0$ and $[N]_0$. For the intensity of the SiN* emission, the peak height of the band origin of the (5,4) transition in the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system at



Fig. 1. Continuum spectra obtained in the systems (a) $N/N_2^* + SiD_4$, (b) $N/N_2^* + SiH_4$. The arbitrary units in both spectra are the same. Experimental conditions: (a) $[SiD_4]_0 = 5 \times 10^{12} \text{ cm}^{-3}$, $[N]_0 = 2.3 \times 10^{14} \text{ cm}^{-3}$, p = 422 Pa, $\overline{u} = 615 \text{ cm} \text{ s}^{-1}$, Z = 12 cm. (b) $[SiH_4]_0 = 9.8 \times 10^{12} \text{ cm}^{-3}$, $[N]_0 = 2.3 \times 10^{14} \text{ cm}^{-3}$, p = 417 Pa, $\overline{u} = 582 \text{ cm} \text{ s}^{-1}$, Z = 5 cm. Spectra were recorded through a Schott glass filter (GG 455). Monochromator split opening 0.2 mm.

409.1 nm was taken, and for Si^{*} emission, the ${}^{3}P \rightarrow {}^{3}P$ line at 252 nm. For constant [N]₀ the results are shown in fig. 2.

The dependence of the maximum intensity of $I(Si^*)$ and $I(SiN^*)$ on $[SiH_4]_0$ was determined in the runs with $[SiH_4]_0$ ranging from 2.0 to 7.0×10^{12} cm⁻³ and $[N]_0 = 2.6 \times 10^{14}$ cm⁻³ by evaluation of a log (intensity) versus log $[SiH_4]_0$ plot. The dependence on $[N]_0$ was determined from similar measurements at $[SiH_4]_0 = 4.5 \times 10^{12}$ cm⁻³ and for various $[N]_0$ ranging from 0.7 to 2.1×10^{14} cm⁻³ (not shown). From these, the dependences

$$I(Si^*) \propto [SiH_4]_0^{1.75 \pm 0.1} [N]_0^{1.1 \pm 0.1}$$

and
$$I(SiN^*) \propto [SiH_4]_0^{1.75 \pm 0.1} [N]_0^{1.1 \pm 0.1}$$

were obtained.

It should be noted in fig. 2 that the maxima of the chemiion current and of the Si* emission coincide, and that they precede the maximum of the SiN* emission intensity. The precursors for the Si* excitation and the chemiionization may be identical. The occurrence of maxima in both the chemiluminescence and the chemiion current suggests that their precursors are reaction intermediates.

The dependence of the continuum emission at 705 nm and around 570–590 nm, and of the N₂^{*} first positive emission at 585 nm (10,6) on Z was measured under $[N]_0 = 2.53 \times 10^{14}$ cm⁻³ and $[SiH_4]_0 = 6.02 \times 10^{12}$ cm⁻³ (*m* = 42). The results are shown in fig. 3 together with the profiles of the SiN* and Si* chemiluminescences. There seems to be a clear distinction in the continuum emission profile between the two



Fig. 2. Profiles of chemiluminescence intensities and the chemiion current in the system SiH₄ + N/N₂^{*}. p = 417 Pa, $\overline{u} = 555$ cm s⁻¹. [N] $_0 = 2.55 \times 10^{14}$ cm⁻³. [SiH₄] $_0$ in 10^{12} cm⁻³: (•) 1.98 (m = 129), (\triangle) 2.56 (m = 100), (\blacktriangle) 2.86 (m = 89), (\bigcirc) 4.13 (m = 62), (\bigtriangledown) 5.69 (m = 45), (\bigtriangledown) 7.05 (m = 36).



Fig. 3. Emission intensity profiles for Si^{*}, SiN^{*}, N^{*}₂ first positive, and the continuum. p = 415 Pa, $\overline{u} = 590 \text{ cm s}^{-1}$. [N]₀ = 2.53 × 10¹⁴ cm⁻³, [SiH₄]₀ = 6.02 × 10¹² cm⁻³ (m = 42). For the N^{*}₂ first positive (N^{*}₂(1+)) and the continuum around 570–590 nm (585 nm), spectra between 550 and 620 nm were recorded from which smooth envelopes were drawn along the continuum to estimate the intensities separately. The N^{*}₂ first positive for Z = 0 cm was recorded in the absence of SiH₄.

selected wavelengths. The emitter of the shorter-wavelength continuum seems to be an important precursor for the reaction. The N_2^* first positive emission shows no abrupt change along the flow tube; it decays roughly exponentially.

3.3. Reaction products

A mass-spectroscopic search for the reaction products was performed using the original reactor. Only H_2 was found. The inner wall of the reactor gradually became covered with a thin metallic-like film. Elemental analysis of the film was not carried out, but according to ref. [6] it consists of $Si_x N_y$. In the first study of this system Dewhurst and Cooper [13] found an approximately stoichiometric formation of H_2 . This was confirmed in the present study. The con-



Fig. 4. Concentration profiles of N, SiH₄ and H₂ in SiH₄ + N/N₂^{*}. The relative concentrations are [N]/[N]₀, [SiH₄]/ [SiH₄]₀, and [H₂]/2[SiH₄]₀. (a) p = 416 Pa, [N]₀ = 2.38 × 10¹⁴ cm⁻³, [SiH₄]₀ = 4.21 × 10¹² cm⁻³ (m = 56). (b) p = 416 Pa, [N]₀ = 2.38 × 10¹⁴ cm⁻³, [SiH₄]₀ = 1.04 × 10¹³ (m = 23). (c) p = 390 Pa, [N]₀ = 1.47 × 10¹⁴ cm⁻³, [SiH₄]₀ = 8.8 × 10¹² cm⁻³ (m = 17).

centration profiles of H_2 and SiH_4 shown in fig. 4b clearly demonstrate an interesting behaviour of this system. The fact that the relation

$[H_2]$ (formed) = 2 [SiH₄] (reacted)

holds at any point on the curve suggests that H_2 is formed almost instantaneously from SiH₄, involving extremely fast elementary processes.

Also remarkable are the [N] profiles shown in fig. 4. Nitrogen atoms as well as SiH₄ were completely consumed in the last two cases (figs. 4b and 4c) even though [N] $_0$ was much greater than [SiH₄] $_0$; m = 23and 17. It is possible that for the first case with m =56 (fig. 4a), both reactants would also be completely consumed further down the reactor. These results indicate that there is a highly efficient "catalytic" N atom removal mechanism coupled to simultaneous removal of SiH_{4} . There seems to be an "induction period" during which a sufficient concentration of the chain initiator is built up. This induction period is mainly a function of reactant concentration. For example, when a very small $[SiH_4]_0 (1.36 \times 10^{12})$ cm^{-3} , m = 175) was used, no consumption of either of the reactants was observable in the reaction time of 50 ms. However, there was some indication that the induction period was also affected by surface conditions.

The effect of O_2 on the reaction was examined. When O_2 at 7.0×10^{12} cm⁻³, the lowest concentration used, was added to the system with [N]₀ = 2.33×10^{14} cm⁻³ and [SiH₄]₀ = 5.73×10^{12} cm⁻³ (m = 41) the chemiluminescence and the chemiionization (except for a slightly enhanced N^{*}₂ first positive emission) were completely suppressed. Under these conditions, no consumption of N atoms or SiH₄ was observable.

The relation between chemiionization, chemiluminescence and concentration profiles should be interesting. An exact comparison cannot be made since the presence of the observation ports for the chemiluminescence and chemiion current prevented an accurate determination of the reaction time in the flow tube. (This is the reason for using Z instead of reaction time in figs. 2 and 3.) However, the volume of the observation ports roughly corresponds to 12 ± 2 cm of the reactor length. A comparison of measured profiles show that the maximum in the SiN* and Si* chemiluminescence occurs at about the reaction time at which roughly 50% of SiH_4 or N atoms have been consumed. This seems reasonable, since at this point the rate of reaction of N atoms with SiH_4 reaches a maximum, and the energy release rate can become also maximum.

3.4. Reaction mechanism

Because of our limited knowledge of this obviously complicated reaction system, no single satisfactory mechanism can be offered at this stage. A plausible mechanism must accommodate the following experimental results: (1) the initial step is slow, (2) both N and SiH₄ disappear simultaneously and very fast, (3) chemiluminescence and chemiionization are observed, and (4) O₂ quenches the system efficiently.

The simultaneous disappearance of N and SiH₄ demands a species which is formed in a chain involving N atoms and reacts in a collision-controlled manner with SiH₄. Silicon- or nitrogen-centered radicals or H atoms are not likely candidates due to the slowness of the respective abstraction reactions. Silicon or nitrogen atoms can be excluded for thermochemical reasons, the abstraction reaction is endothermic. A possible species fulfilling the above requirement could be $N_2(A^3\Sigma_u^+)$, reacting with SiH₄ according to

$$N_2(A^{3}\Sigma_{u}^{+}) + SiH_4 \rightarrow SiH_4(^{3}T_2) + N_2(^{1}\Sigma_{g}^{+}).$$
 (1)

Reaction (1) could very well be the initiation step, too, which may be slow due to the low concentration of $N_2(A^3\Sigma_u^+)$ in active nitrogen [14].

The excited silane can decompose in two ways, either by splitting off a hydrogen atom or a hydrogen molecule. Both SiH_3 and SiH_2 in their lowest triplet states are likely to react very rapidly with N atoms.

The following steps are postulated for the case of SiH₂:

$$SiH_4({}^{3}T_2) \rightarrow SiH_2({}^{3}B) + H_2,$$
 (2)

$$SiH_2(^{3}B) + N \rightarrow SiN + H_2$$

$$\Delta H > -385 \pm 63 \text{ kJ mol}^{-1}, \tag{3}$$

$$\mathrm{SiN} + \mathrm{N} + \mathrm{M} \to \mathrm{SiN}_2 + \mathrm{M},\tag{4}$$

$$\operatorname{SiN}_2 + \operatorname{N} \to \operatorname{SiN} + \operatorname{N}_2(\operatorname{A}{}^3\Sigma_u^+).$$
(5)

Steps (4) and (5) are analogous to a mechanism proposed for the active nitrogen $-C_2H_2$ system by Kistiakowsky and co-workers [15]. The SiN* chemiCHEMICAL PHYSICS LETTERS

luminescence may be explained by step (3), whose exothermicity is sufficient for the SiN* excitation at 370 nm (E = 323 kJ mol⁻¹). In addition, this mechanism explains the formation of two molecules of hydrogen for every silane destroyed, and the Si_xN_y wall deposit. The formation of Si atoms can be accounted for by including the following steps:

$$SiN + N \rightarrow Si + N_2, \tag{6}$$

$$\mathrm{Si} + \mathrm{N}_2 + \mathrm{M} \to \mathrm{Si}\mathrm{N}_2 + \mathrm{M}. \tag{7}$$

Reaction (7) has been observed to occur in a matrix at 4 K [16]. The Si* chemiluminescence may be generated as a result of the two-body collision:

$$Si + N_2^*(A^3\Sigma_u^+) \to Si^* + N_2.$$
 (8)

This same process could lead to the ionization of Si atoms as well, since the ionization potential of Si, 8.15 eV, lies below the dissociation energy of N_2 , 9.7 eV.

 O_2 may intervene in almost every step of the mechanism and so the large effect on product formation is understandable.

A mechanism initiated by the formation of SiH₃, on the other hand, is less favourable. The molecule HSiN which should be formed in the reaction of N with SiH₃ in accordance with (3) is not the stable isomer of this molecule [17]. With the stable form SiNH, the elementary steps corresponding to (3)–(5) would be much less probable. Furthermore the chain carrier SiH which has been detected under somewhat different conditions by its chemiluminescence has not been found in the present study [18].

The above mechanism does not provide any clues to the two carriers of the continuum emission. If the continuum emission actually consists of unresolved bands the emitter must be at least a triatomic species consisting of heavy constituents only. The known absorption spectrum rules out SiN_2 as a possible candidate [16]. Furthermore the mechanism does not give the correct dependence of $I(Si^*)$ and $I(SiN^*)$ on [N]₀ and $[SiH_4]_0$. If one assumes a direct proportionality for $I(Si^*)$ and $I(SiN^*)$ to [Si] and [SiN], respectively, then the mechanism predicts a stronger dependence on $[N]_0$ than on $[SiH_4]_0$ (mainly due to reaction (1)), contrary to the experimental findings. In terms of a pure radical chain mechanism, it is hard for us to propose any other reaction in place of (1). However, if ion-molecule reactions play a role, this difficulty could be overcome.

References

- [1] W. Jevons, Proc. Roy. Soc. 89A (1914) 187.
- [2] R.S. Mulliken, Phys. Rev. 26 (1925) 319.
- [3] F.A. Jenkins and H. de Laszlo, Proc. Roy. Soc. 122A (1929) 103.
- [4] K. Schofield and H.P. Broida, Photochem. Photobiol. 4 (1965) 989.
- [5] H. Bredohl, I. Dubois, Y. Houbrechts and M. Singh, Can. J. Phys. 54 (1976) 680.
- [6] L. Bárdos, J. Musil and M. Lubanski, Czech. J. Phys. B34 (1984) 1242.
- [7] O. Horie, P. Potzinger and B. Reimann, to be submitted.
- [8] H. Hoffmeyer, O. Horie, P. Potzinger and B. Reimann, J. Phys. Chem. 89 (1985) 2901.
- [9] C.R. Gaty, R.A. Young and R.L. Sharpless, J. Chem. Phys. 39 (1963) 1234.
- [10] R.A. Young and G. St. John, J. Chem. Phys. 45 (1966) 4156.
- [11] LJ. Radziemski Jr. and K.I. Andrew, J. Opt. Soc. Am. 55 (1965) 474.
- [12] A. Fontijn and P.H. Vree, Symp. (Intern.) Combust. 11 (1967) 343.
- [13] H.J. Dewhurst and G.D. Cooper, J. Am. Chem. Soc. 82 (1960) 4220.
- [14] M.F. Golde and B.A. Thrush, Rept. Progr. Phys. 36 (1973) 1285.
- [15] C.A. Arrington Jr., O.O. Bernardini and G.B. Kistiakowsky, Proc. Roy. Soc. A310 (1969) 161.
- [16] R.R. Lembke, R.F. Ferrante and W. Weltner Jr., J. Am. Chem. Soc. 99 (1977) 416.
- [17] R. Preuss, R.J. Buenker and S.D. Peyerimhoff, J. Mol. Struct. 49 (1978) 171.
- [18] M. Delf and P. Potzinger, unpublished results.