

The reaction between silylene and ammonia: some gas-phase kinetic and quantum chemical studies.

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Abstract

Time-resolved kinetic studies of the reaction of silylene, SiH₂, generated by 193 nm laser flash photolysis of silacyclopent-3-ene, have been carried out in the presence of ammonia, NH₃. Second order kinetics were observed. The reaction was studied in the gas phase at 10 Torr total pressure in SF₆ bath gas at each of the three temperatures, 299, 340 and 400 K. The second order rate constants (laser pulse energy of 60 mJ/pulse) fitted the Arrhenius equation:

$$\log(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-10.37 \pm 0.17) + (0.36 \pm 1.12 \text{ kJ mol}^{-1})/RT \ln 10$$

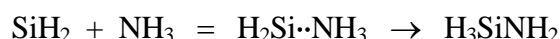
Experiments at other pressures showed that these rate constants were unaffected by pressure in the range 10-100 Torr, but showed small decreases in value at 3 and 1 Torr. There was also a weak intensity dependence, with rate constants decreasing at laser pulse energies of 30 mJ/pulse. Ab initio calculations at the G3 level of theory, show that SiH₂ + NH₃ should form an initial adduct (donor-acceptor complex), but that energy barriers are too great for further reaction of the adduct. This implies that SiH₂ + NH₃ should be a pressure dependent association reaction. The experimental data are inconsistent with this and we conclude that SiH₂ decays are better explained by reaction of SiH₂ with the amino radical, NH₂, formed by photodissociation of NH₃ at 193 nm. The mechanism of this previously unstudied reaction is discussed.

Introduction

Silylenes are of importance because they are implicated in the thermal and photochemical breakdown mechanisms of silicon hydrides and organosilanes, as well as being key intermediates in CVD. Time resolved kinetic studies, carried out in recent years, have shown that the simplest silylene, SiH₂, reacts rapidly and efficiently with many chemical species.^{1,2} Examples of its reactions include Si-H bond insertions, C=C and C≡C π-bond additions.³ SiH₂ also has a great affinity for electronegative elements and will react with lone pair donor species containing the elements of N, O, F, P, S and Cl amongst others⁴. We, and others, have recently studied the kinetics of its reactions with “O-donor” molecules, H₂O^{5,6}, CH₃OH (CD₃OD)⁵, Me₂O^{7,8}, Me₂CO⁹, MeCHO^{10,11}, CO¹², CO₂¹³ and O₂¹⁴ itself, and also with “Cl-donor” molecules, HCl¹⁵ and CH₃Cl¹⁶. We have also previously reported kinetic studies of the reactions of SiH₂ with the N-containing molecules N₂O¹⁷, NO¹⁸ and even N₂¹⁹ (although no reaction was found in this case). None of these can be represented as typical reactions of a silylene with the nitrogen lone pair. We therefore set out to investigate the prototype reaction of SiH₂ with NH₃. This reaction has the added importance in that it may be considered as a model for some of the likely reaction steps involved in producing solid materials such as Si₃N₄²⁰.

There is no previous experimental study of this reaction. At the outset of this work we were aware of the potential problem of substrate absorption at the UV photolysis wavelength (193nm) required for generation of SiH₂ from our precursor (silacyclopent-3-ene). NH₃ has an absorption band ($\tilde{A}^1A_2'' \leftarrow \tilde{X}^1A_1$) in the wavelength region 170 – 217 nm²¹. Whether this would give rise to kinetic complications was not predictable in the absence of knowledge of the rate constants for the reaction under consideration. We therefore decided to press ahead with the study and evaluate the findings. Earlier theoretical work by Raghavachari et al⁴ gives some guidance as to what to expect. Calculations at the MP4 level with allowance for electron correlation effects, indicate a mechanism involving initial formation of a donor acceptor adduct

followed by rearrangement by 1,2 H-migration to give the formal insertion product, silylamine, viz:



The donor acceptor complex was bound by some 105 kJ mol^{-1} and the rearrangement barrier calculated to be *ca* 54 kJ mol^{-1} above the reactant energy⁴. By analogy with findings for $\text{SiH}_2 + \text{H}_2\text{O}$ ^{5,6} which has a similar reaction mechanism (and calculated potential energy surface) this suggests that the $\text{H}_2\text{Si}\cdot\text{NH}_3$ adduct will be the effective final product under experimental conditions (short timescale/moderate temperatures) because the rearrangement barrier for $\text{H}_2\text{Si}\cdot\text{NH}_3$ to H_3SiNH_2 is too high. Stable donor acceptor adducts of silylenes with N-type lone pair donors have been detected in low temperature matrices^{22,23}. The expectation here is therefore of an association reaction, which should require third body assistance to stabilise the initially formed vibrationally excited adduct. This implies pressure dependent second order kinetics. We describe here the results of an attempted experimental kinetic study, together with further theoretical calculations aimed at refining the energy surface of this reaction.

Experimental Section

Equipment, Chemicals and Method. The apparatus and equipment for these studies have been described in detail previously^{24,25}. Only essential and brief details are therefore included here. SiH_2 was produced by the 193 nm flash photolysis of silacyclopent-3-ene (SCP) using a Coherent Compex 100 exciplex laser. Photolysis pulses (beam cross section $4 \text{ cm} \times 1 \text{ cm}$) were fired into a variable temperature quartz reaction vessel with demountable windows, at right angles to its main axis. SiH_2 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Rhodamine 6G. The monitoring laser beam was multipassed 36 times along the vessel axis, through the reaction zone, to give an effective path length of 1.5 m. A portion of the monitoring

beam was split off before entering the vessel for reference purposes. The monitoring laser was tuned to 17259.50 cm^{-1} , corresponding to the known ${}^R Q_{0,J}(5)$ strong rotation transition^{24,26} in the $\text{SiH}_2 \tilde{A}^1\text{B}_1(0,2,0) \leftarrow \tilde{X}^1\text{A}_1(0,0,0)$ vibronic absorption band. Light signals were measured by a dual photodiode/differential amplifier combination and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of between 3 and 15 photolysis laser shots (at a repetition rate of 0.5 or 1 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a non-linear least squares package. This analysis provided the values for first-order rate coefficients, k_{obs} , for removal of SiH_2 in the presence of known partial pressures of substrate gas.

Gas mixtures for photolysis were made up, containing between 3.1 and 4.2 mTorr of precursor (SCP), variable pressures of NH_3 between 30 and 300 mTorr, and inert diluent, SF_6 , up to total pressures between 1 and 100 Torr (although mainly 10 Torr[†]). Pressures were measured by capacitance manometers (Chell, Barocel). All gases used in this work were frozen and rigorously pumped to remove any residual air prior to use. SCP was a gift from the group of Professors Nefedov and Egorov. After redistillation, GC analysis showed it was >85% pure. NH_3 (99.98%) was from BOC. Sulfur hexafluoride, SF_6 , (no GC-detectable impurities) was from Cambrian Gases. GC purity checks were carried out with a 3 m silicone oil column (OV101) operated at 60°C . N_2 was used as carrier gas and detection was by FID. Detection limits for hydrocarbon impurity peaks were better than 0.1% of the principal component.

Ab Initio Calculations. The electronic structure calculations were performed with the Gaussian 98 software package²⁷. All structures were determined by energy minimization at the MP2=Full/6-31G(d) level. Transition State structures were characterised as first order saddle points by calculation of the hessian matrix. Stable structures, corresponding to energy minima, were identified by possessing no negative eigenvalues of the Hessian, whilst transition states

[†] 1 Torr = 133.3 Nm^{-2}

were identified by having one and only one negative eigenvalue. The standard Gaussian-3 (G3) compound method²⁸ was employed to determine final energies for all local minima. For transition states the elements of the G3 method were used, viz: optimization to TS at HF/6-31G(d), frequencies at HF/6-31G(d), optimization to TS at MP2=full/6-31G(d), followed by four single point energy determinations at the MP2=full/6-31G(d) geometry, viz: QCISD(T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2=full/G3large, and the values were combined according to the G3 procedure.²⁸ The identities of the transition state structures were verified by calculation of Intrinsic Reaction Co-ordinates²⁹ (IRC) at the MP2=Full/6-31G(d) or B3LYP/6-31G(d) levels. Reaction barriers were calculated as differences in G3 enthalpies at 298.15 K. In addition to these calculations, two further calculations were carried out at the MP2=full/6-31G(d,p) and MP2=full/6-311++G(2d,2p) levels in order to test the effects of larger basis sets.

Results

Preliminary Experiments. The gas phase UV spectrum of NH₃ was recorded over the wavelength range, 190 – 220 nm. The characteristic vibrational progression of the $\tilde{A} \leftarrow \tilde{X}$ system was observed²¹ and the decadic extinction coefficient at 193nm was calculated to be 985 dm³ mol⁻¹ cm⁻¹ in reasonable agreement with the literature²¹. At the partial pressures of NH₃ employed in these experiments this means that up to 10% of the 193 nm laser pulse is absorbed by the substrate. SCP has a non-structured UV spectrum in this region with increasing absorbance at shorter wavelengths; the extinction coefficient at 193 nm is 967 dm³ mol⁻¹ cm⁻¹. Because the partial pressures of SCP are much lower, the fractional light absorption is much less. Although photodecomposition of NH₃ is known to occur (see discussion) at 193 nm, blank experiments at the SiH₂ detection wavelength (*ca* 579 nm), showed no detectable transient absorption from NH₃ photolysis alone.

Kinetics. Preliminary experiments established that, for a given reaction mixture, decomposition decay constants, k_{obs} , were not dependent on the exciplex laser energy within the normal routine range of variation (50-70 mJ/pulse). However there was some systematic variation at lower pulse energies (see below). There was no dependence on the number of photolysis laser shots (up to 15 shots). The constancy of k_{obs} (3 shot averages) showed that there was no effective depletion of reactants. Higher pressures of precursor were required at the higher temperatures because signal intensities decreased with increasing temperature. However, for the purposes of rate constant measurement at a given temperature the precursor pressure was kept fixed. At each temperature of study, a series of experiments was carried out to investigate the dependence of k_{obs} on NH_3 pressure. The results of these experiments are shown in Figures 1 and 2. Reasonable linear fits were obtained, as expected for second order kinetics, although it should be noted that there is slightly higher scatter than is usually obtained in this kind of study⁵⁻¹⁸. Because the rate constants showed a dependence on laser pulse energy, two plots are shown, one for higher pulse energies (60 mJ) and one for lower values (*ca* 30 mJ). Similar plots (not shown) were obtained for data recorded at 400 K. The second order rate constants derived from the gradients of these plots by least squares fitting, are shown in Table 1. The error limits (precision) are single standard deviations. It can be seen that, for a given laser pulse energy, the rate constants are the same at each temperature within experimental error, although a small variation with temperature cannot be ruled out. Because the scatter of data increased with temperature, further experiments at higher temperatures were not carried out. An Arrhenius plot of the rate constants (at laser energies of 60 mJ/pulse) yielded the equation:

$$\log(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (-10.37 \pm 0.17) + (0.36 \pm 1.12 \text{ kJ mol}^{-1})/RT \ln 10$$

The error limits are based on the spread of each individual rate constant.

In addition to these experiments, some runs were carried out at other total pressures in the range 1 to 100 Torr (SF_6) at the higher laser pulse energy. These were generally single point

determinations. The results are shown in Table 2. It was assumed that the uncertainties were 10%, ie slightly greater than the standard deviations of the second order plots. Examination of the values shows that there is no discernable pressure dependence of the rate constants above 10 Torr at any temperature. Below 10 Torr, there is a slight fall off in values.

The dependence of k_{obs} on laser intensity was studied as a possible aid to unravelling the mechanism. In the practical range of study (25 to 120 mJ/pulse), the only detectable variation occurred between 30 and 60 mJ/pulse. These results are already shown in Table 1. Above 60 mJ/pulse, values of k_{obs} (not shown) were rather scattered although not detectably larger in magnitude.

Ab Initio Calculations. Possible species of the SiH_3N family were explored in some detail at the G3 level of theory and are shown on the potential energy surface (PES) in Figure 3. A fairly straightforward surface and set of species has been found. This comprises three local minima (ie stable intermediates or products), apart from the reactants, $\text{SiH}_2 + \text{NH}_3$, and three transition states. The lowest energy reaction pathway may be described as follows. The initial step forms the donor-acceptor complex (ylid), $\text{H}_2\text{Si}\cdots\text{NH}_3$, which can then either undergo a nitrogen-to-silicon H-shift via TS1 to form silylamine, SiH_3NH_2 , or decompose via TS2 to give aminosilylene, HSiNH_2 , by H_2 elimination (a 4-centre process). HSiNH_2 can also be formed directly from SiH_3NH_2 by H_2 elimination from silicon (a 3-centre process) via TS3. It should be noted that, to reach either SiH_3NH_2 or HSiNH_2 , the reactants have to overcome positive energy barriers. The structures of the intermediate species, products and reaction transition states are shown in Figure 4 and the enthalpy values are listed in Table 3. Further calculations of the energies of these species with larger basis sets showed small changes in values (listed in Table 3) but do not give rise to any different mechanistic expectations.

Additionally we have explored briefly a few species on the SiH_4N potential energy surface (G3 level only). These consist of the aminosilyl radical, H_2SiNH_2 , and its possible decomposition

products, $\text{SiH}_2 + \text{NH}_2$, $\text{HSiNH}_2 + \text{H}$ and $\text{H}_2\text{Si}=\text{NH} + \text{H}$. The enthalpy values for these are included in Table 3. It should be noted that starting from $\text{SiH}_2 + \text{NH}_2$, all possible pathways are exothermic.

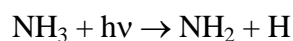
Discussion

Evaluation of the kinetics. The experimental objective of this study was to investigate the kinetics of reaction of silylene in the presence of ammonia, in the hope of obtaining absolute values of rate constants for the elementary reaction, $\text{SiH}_2 + \text{NH}_3$. The first objective has been achieved, and the kinetic results have characteristics strongly resembling those of a typical SiH_2 reaction. Second order kinetics has been established. The magnitude of the rate constants is quite high. There is only a very slight temperature dependence of the rate constants, with a negative activation energy. The Arrhenius parameters look reasonable. The measured value for $\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ of -10.37 compares favourably with the range, -9.88 to -12.09 , found for other silylene reactions (see ref 14, Table 7 for the most recent values). The value for the activation energy of $-0.36 \pm 1.12 \text{ kJ mol}^{-1}$ is close to the range, -1.6 to -4.5 kJ mol^{-1} , of most silylene reactions. There are however two features which tend to suggest that the kinetics are not those of the simple reaction, $\text{SiH}_2 + \text{NH}_3$. The first is that of the lack of overall pressure dependence, except at low pressures. It is overwhelmingly likely that the true reaction of SiH_2 with NH_3 is an association process, in which case a pressure dependent reaction should be expected. This is discussed in more detail below. The second feature is that of the dependence of the rate constants on laser intensity. If the reaction of SiH_2 is with substrate alone, there should be no such dependence. This was verified by us for the reaction $\text{SiH}_2 + \text{Me}_2\text{CO}$ ⁹. If there are reactions of SiH_2 with radicals or other intermediates, then intensity dependences of the apparent rate constants can arise. We found this in our study of $\text{SiH}_2 + \text{CH}_3\text{Cl}$ ¹⁶.

Ab initio calculations for SiH₂ + NH₃ and further mechanistic considerations. The earlier theoretical calculations of Raghavachari et al⁴ revealed a donor acceptor adduct with a binding energy (well depth) of 105 kJ mol⁻¹ and a barrier to rearrangement of 54 kJ mol⁻¹ (above the reaction threshold). The results obtained here at the higher G3 level, are in reasonable accord with this, although the rearrangement barrier is slightly lower. The barrier is still high enough, however, to make surmounting it impossible under experimental conditions³⁰. We have extended the earlier work, by the discovery of the H₂ elimination pathway from the adduct leading directly to HSiNH₂. However this also has a sufficiently high energy barrier to make it very unlikely that this process can occur here either. It is worth noting that H₂ elimination pathways have also been found from the adducts of SiH₂ with H₂O^{5,6} and with HCl¹⁵, although only in the latter case is the step thought to be occurring under experimental conditions. This means that, unless there is a hitherto unidentified pathway, the effective final reaction product should be the adduct, H₂Si·NH₃. This is the situation found previously for the reaction system, SiH₂ + H₂O, where H₂Si·OH₂ was the final product⁶. Since SiH₂ + NH₃ → H₂Si·NH₃ is an association process, the question arises as to what extent it should be pressure dependent, ie what is the magnitude of the third body effect at 298 K? Although in principle this could be calculated using RRKM theory, there is sufficient literature information to make a reasonable estimate. The system under study here, lies between those of SiH₂ + H₂O (well depth = 54-65 kJ mol⁻¹)^{5,6} and SiH₂ + C₂H₄ (well depth = 187 kJ mol⁻¹)³¹. The main determinant of the extent of pressure dependence is the binding energy, ie well depth, although molecular size also affects it. In the SiH₂ + H₂O system, the rate constant in 10 Torr of SF₆ (1.4 × 10⁻¹² cm³ molecule⁻¹ s⁻¹) is at least two orders of magnitude below the high pressure limiting value and the variation between 10 and 100 Torr is a factor of 3.6. In the SiH₂ + C₂H₄ system, the rate constant at 10 Torr of SF₆ (1.58 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) is a factor of 2.2 below the high pressure limiting value and the variation between 10 and 100 Torr is a factor of 1.8 (and a further factor of 2.3 between 1 and 10 Torr). The

parameters of the $\text{SiH}_2 + \text{NH}_3$ system are closer to those of $\text{SiH}_2 + \text{H}_2\text{O}$ than $\text{SiH}_2 + \text{C}_2\text{H}_4$ meaning that we would anticipate rate constants at least an order of magnitude below the high pressure limiting value and a variation with pressure of a factor of 2 to 3 between 10 and 100 Torr and larger than this between 1 and 10 torr. Although there is some uncertainty in these estimates, the observed pressure dependence at 299 K is almost nothing, ie nowhere near to this. It therefore seems very unlikely that we are observing the reaction $\text{SiH}_2 + \text{NH}_3$. The true values for the second order rate constants of this reaction are almost certainly smaller than we are observing probably by as much as an order of magnitude (at 10 Torr). It is also probable that a catalysed process, involving two molecules of NH_3 , by analogy with findings in the $\text{SiH}_2 + \text{H}_2\text{O}$ reaction system³², would contribute to SiH_2 removal. The non-observation of a quadratic dependence of k_{obs} on $[\text{NH}_3]$ can therefore be taken as further evidence against the direct reaction of SiH_2 with NH_3 . The nature of the removal process for SiH_2 is discussed in the next section.

Radical reactions and the removal mechanism for SiH_2 . Photodecomposition of NH_3 is likely to be the main cause of complexity in this study, viz.



At both 184.9 and 206.2 nm the quantum yield for this process is near unity²¹. It is almost certainly similar at 193 nm. With a fairly high extinction coefficient at 193 nm, this means that high instantaneous concentrations of NH_2 radicals will be formed. Because of the high ratio of substrate to SCP, instantaneous NH_2 concentrations will be well in excess of those of SiH_2 and could be as much as 10% of those of NH_3 in the reaction zone. It is also worth noting that at high NH_3 partial pressures (> 200 mTorr) there is a significant decrease in initial SiH_2 signal intensity suggesting increased competition for the excitation pulse by the substrate. Thus it seems very probable that SiH_2 is being removed by reaction with NH_2 , viz



Although nothing is known experimentally about this reaction, a reaction between silylene and a radical is expected to be barrierless (our calculations have shown that the species are spontaneously attracted from approach distances of 3 Å). The initially formed aminosilyl radical will have vibrational energy well in excess of that needed to decompose by H atom expulsion (see energetics of Table 3) and should form aminosilylene, HSiNH₂, although formation of isomeric H₂Si=NH is also energetically possible. This is important because it means that reaction between SiH₂ and NH₂ will not be pressure dependent.

With [NH₂] in excess over [SiH₂], pseudo first order kinetics for SiH₂ should be maintained, as observed. Although NH₂ radical recombination might be expected to deplete initial NH₂ concentrations, it is a pressure dependent association process²¹ and should not compete significantly. This may be the reason why the dependence of the rate constants on laser intensity is not very great. Normally one would expect radical-radical reactions to be more significant at high light intensities than at low light intensities. But if NH₂ recombination is slow, [NH₂] may decrease rather slowly on the experimental time scale and it can maintain an approximate proportionality with [NH₃]. Nevertheless some dependence on intensity, as observed, is a sign of reaction between two transient species. The greater than normal scatter in the data is also an indicator of more complex kinetics.

The fate of H atoms is another potential cause of complexity. Reaction of H with NH₃ is very slow²¹, and so reaction of H with SCP seems probable. However this will only occur after formation of SiH₂ and therefore not affect the kinetics. Even if SCP is largely consumed in the reaction zone as a consequence, it will be replenished by diffusion between shots (as shown by the test for depletion).

Conclusion

Under the conditions of the present experiments, silylene is removed by reaction, not with NH_3 , but rather by NH_2 , formed by the 193 nm photodissociation of NH_3 . To study the elementary $\text{SiH}_2 + \text{NH}_3$ reaction will require an SiH_2 precursor whose decomposition occurs outside the NH_3 absorption wavelength region (viz 170 – 220 nm).

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Table 1. Experimental second-order rate constants for the SiH₂ + NH₃ system at three temperatures and two laser pulse energies.

<i>T</i> /K	<i>k</i> ^a (60 mJ/pulse)	<i>k</i> ^a (30 mJ/pulse)
299	4.78 ± 0.25	3.87 ± 0.22
340	5.06 ± 0.45	4.09 ± 0.49
400	4.62 ± 0.43	3.21 ± 0.60

^aUnits: 10⁻¹¹ cm³ molecule⁻¹ s⁻¹

Table 2. Pressure dependence of experimental second-order rate constants for the SiH₂ + NH₃ system at three temperatures (laser pulse energy: 60 mJ)

<i>T</i> /K	<i>P</i> (SF ₆)/Torr	<i>k</i> /10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
299	1.2	3.47 ± 0.35
	3.0	4.30 ± 0.43
	10.0	4.78 ± 0.25
	30.2	4.70 ± 0.47
	100.4	4.67 ± 0.47
340	1.2	3.07 ± 0.31
	3.5	4.36 ± 0.44
	10.0	5.06 ± 0.45
	30.7	4.43 ± 0.44
	73.0	4.73 ± 0.47
400	10.0	4.62 ± 0.45
	30.8	4.49 ± 0.45
	101.8	4.90 ± 0.49

Table 3. Ab Initio enthalpies for SiH₅N species of interest in the reaction of SiH₂ with NH₃ and also SiH₄N species of interest in the reaction of SiH₂ with NH₂

Molecular species	Energy/hartree(G3)	Relative energy/kJ mol ⁻¹		
		G3	MP2P ^a	MP2DP ^b
SiH ₂ + NH ₃	-346.956923	0	0	0
H ₂ Si··NH ₃ ylid	-346.997317	-106	-121	-104
TS1	-346.943760	35	34	38
TS2	-346.949134	20	25	25
H ₃ SiNH ₂	-347.058969	-267	-277	-272
TS3	-346.962400	-14	4	-4
H ₂ + HSiNH ₂	-347.001548	-117	-128	-115
SiH ₂ + NH ₂	-346.288122	0	-	-
H ₂ SiNH ₂	-346.415466	-334	-	-
HSiNH ₂ + H	-346.336123	-126	-	-
H ₂ Si=NH + H	-346.311997	-63	-	-

^a MP2=full/6-31G(d,p) ^b MP2=full/6-311++G(2d,2p)

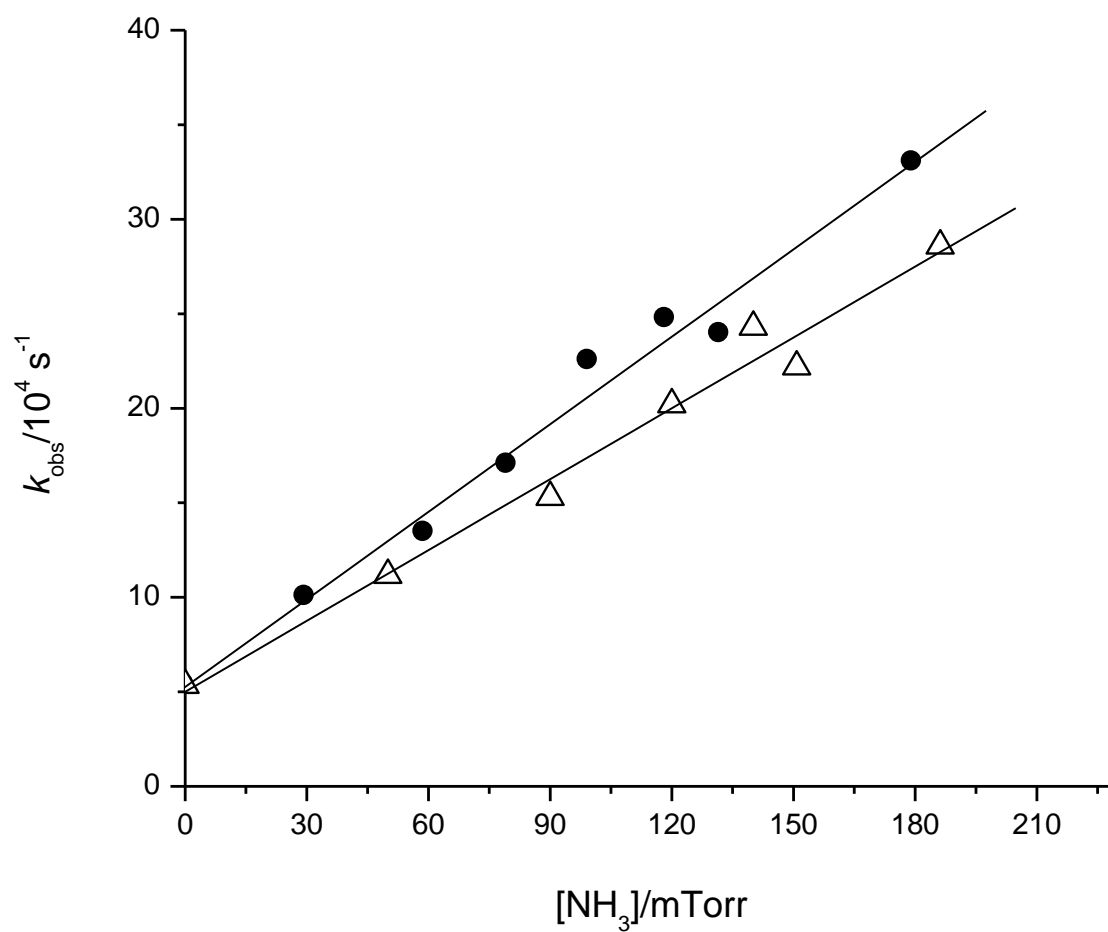


Figure 1. Second-order plot for reaction of SiH_2 with NH_3 at 10 Torr total pressure (SF_6) and 299 K. Laser pulse energies: ●, 60 mJ; △, 30 mJ.

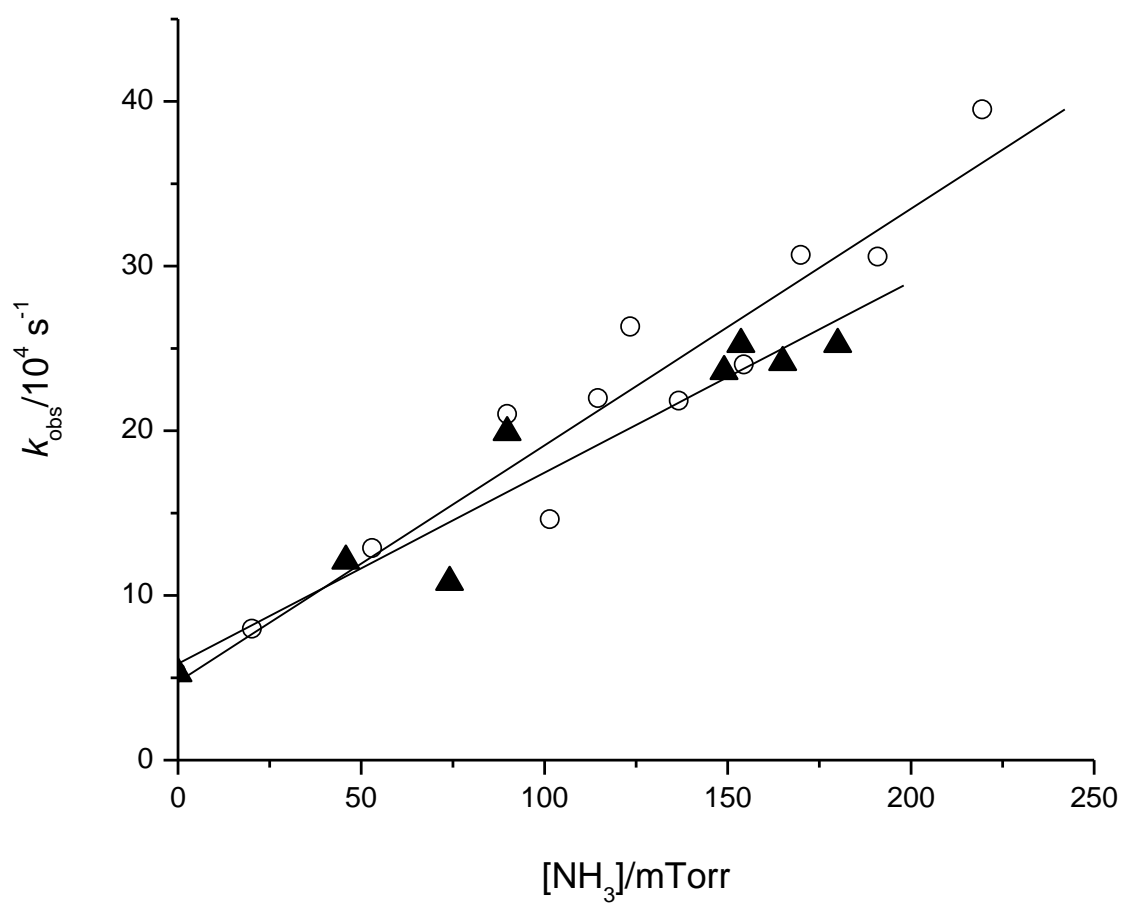


Figure 2. Second-order plot for reaction of SiH_2 with NH_3 at 10 Torr total pressure (SF_6) and 340 K. Laser pulse energies: O, 60 mJ; ▲, 30 mJ.

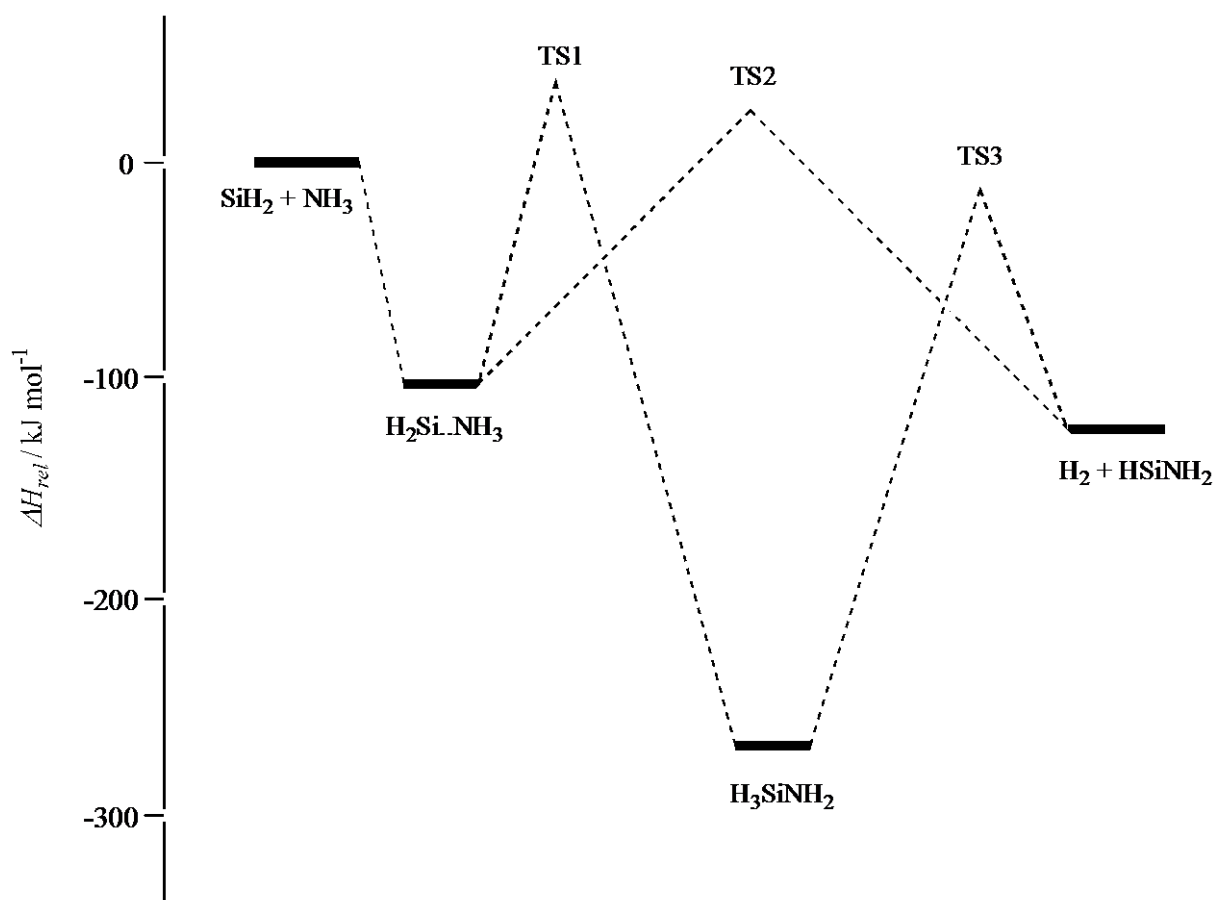


Figure 3. Potential energy (enthalpy) surface for the reaction of $\text{SiH}_2 + \text{NH}_3$. All enthalpies are calculated at the G3 level.

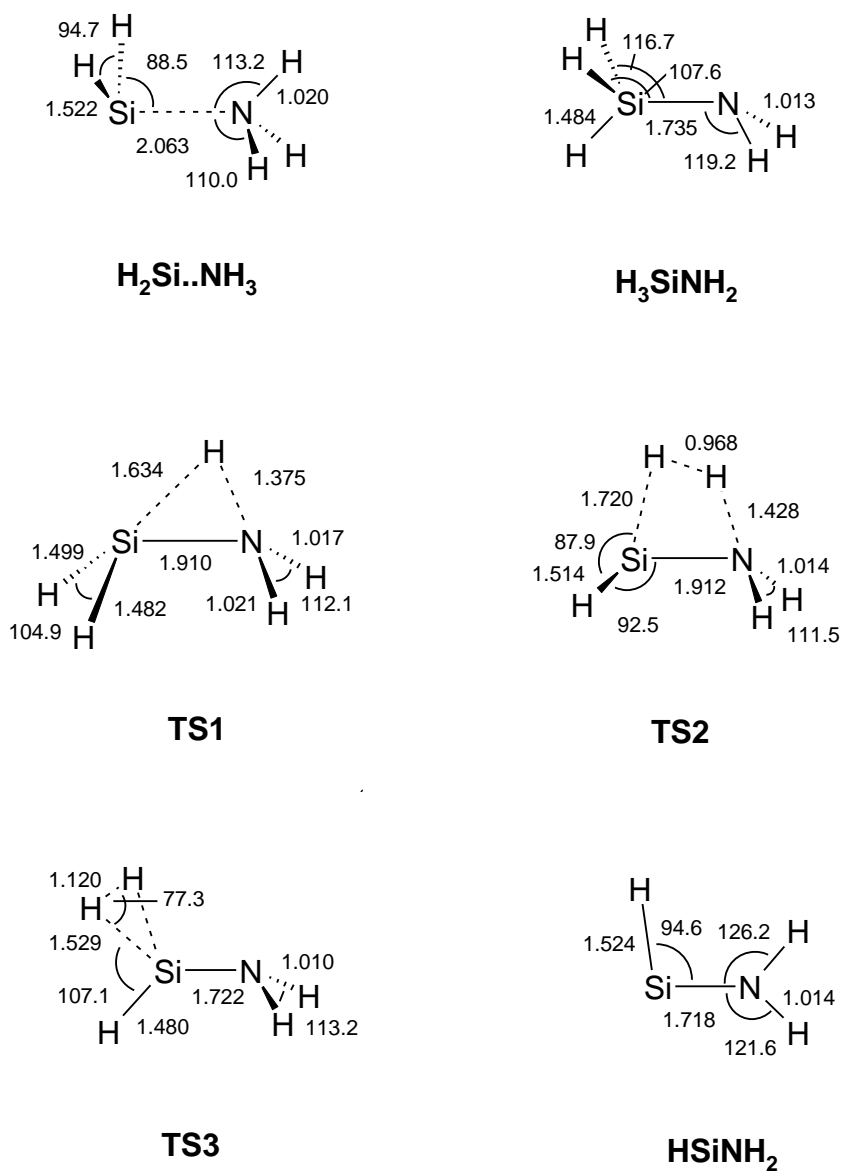


Figure 4. Ab initio MP2 = full/6-31G(d) calculated geometries of local minimum structures and transition states on the SiH₂ + NH₃ energy surface. Selected distances are given in Å and angles in degrees.