batical leave to carry out this work. We thank Dr. J. Finkenbine for the measurement of the mass spectra.

Registry No. 2, 102493-41-4; $PhSiD_3$, 18164-03-9; (p-tol)SiH_3, 931-70-4; $PhSiH_3$, 694-53-1; (n-hexyl)SiH_3, 1072-14-6; (benzyl)SiH_3, 766-06-3; (cyclohexyl)SiH_3, 18162-96-4; $PhMeSiH_2$, 766-08-5; Cp_2TiMe_2, 1271-66-5; D_2, 7782-39-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 3-methylcyclohexene, 591-48-0; 4-methylcyclohexene, 591-47-9; norbornene, 498-66-8; 2-pentene, 109-68-2; 1-pentene, 109-67-1; styrene, 100-42-5.

Theoretical and Experimental Studies of the Flash Pyrolysis of Trimethylsilyl Azide and Trimethylgermyl Azide: Generation and He I Photoelectron Spectra of Iminosilylene and Iminogermylene

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Received July 17, 1986

The generation and the detection of iminosilylene and its germanium analogue from trimethylsilyl (and germyl) azide by gas-phase flash pyrolysis (1100 K, 10^{-2} mbar) are described. The ab initio study of molecular rearrangements of the $(CH_3)_3SiN_3$ pyrolysis product after loss of N_2 predicts the possible formation of several compounds with the probability order $(CH_3)_2HSiN{=}CH_2 > Si{\equiv}NH + C_3H_8 > (CH_3)_2HSiCH{=}NH \gg Si{\equiv}NCH_3 + C_2H_6$. The comparison of the experimental and theoretical values of the first ionization potentials of the possible pyrolysis products indicates the formation of transient metallaisonitrile analogues $M{\equiv}NH$ (M = Si, Ge; iminosilylene and iminogermylene) and, in the case of the silyl derivative, of the imine $(CH_3)_2HSiN{=}CH_2$.

Introduction

The chemistry of unsaturated organometallic compounds with multiple bonds between a group 14 atom (except carbon) and a heteroatom has assumed increasing importance during the last several years, as shown by the large number of reviews[2-10] dealing with both theoretical and experimental aspects. The existence of these entities was proposed primarily on the basis of products obtained by chemical trapping. Relatively little work, however, has dealt with their isolation, since most are unstable and highly reactive. There exist only a limited number of spectroscopic data on this family, mostly generated in studies using argon matrix infrared spectroscopy for $R_2Si{=}O$[11-13] and $Si{\equiv}NH$,[14] mass spectroscopy for $R_2Si{=}S$,[15] and UV photoelectron spectroscopy for silane- and germanethiones,[16,17] germanone,[17,18] (phenylimino)silylene (phenylsilaisonitrile)[19] and various diatomic molecules such as SiO, GeO, GeS, GeSe, SnS, SnTe, and PbTe.[20-23] Most of these compounds were obtained by gas-phase flash pyrolysis from appropriate precursors. When the heteroatom was nitrogen, azides were found to be the most suitable precursors and thus the most often used[2,19,24,25] since they lose a nitrogen molecule relatively easy.

By analogy with results obtained by photolysis (in solution) and chemical trapping,[24,26-30] our initial aim was

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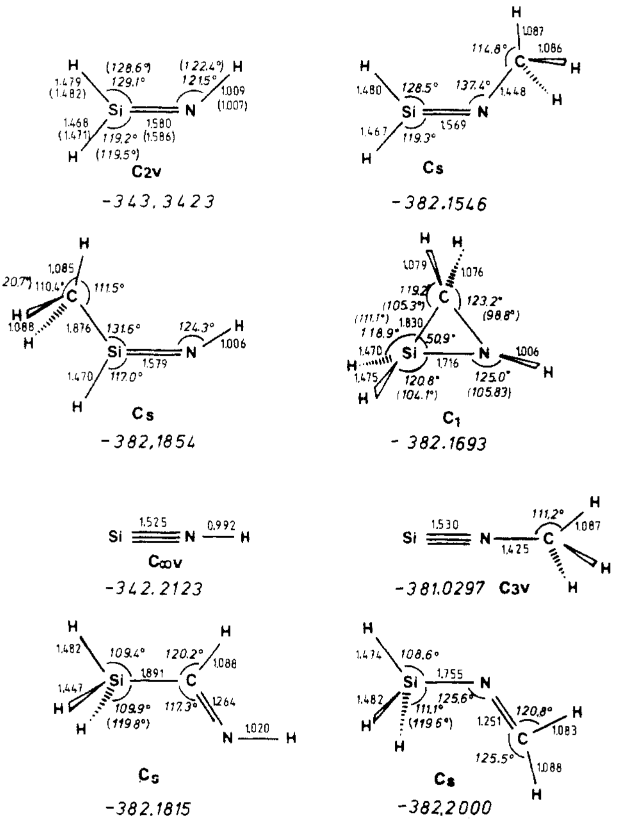

Figure 1. Calculated (3.21G*) structures (Å, d^0) and total energies (hartree) of possible pyrolysis products of methylsilyl azide. The values in parentheses about the silanimine are from the ref 42. In the other molecules the values in parentheses are the dihedral angles defined by the bond and the plane of the page.

to define the electronic characters of silan- and germanimines $R_2M{=}NR'$ (M = Si, Ge). To this end, we have subjected trimethylsilyl azide and trimethylgermyl azide to thermal degradation in order to identify the products formed, using their ionization potentials as determined by photoelectron spectroscopy (eq 1).

$$(CH_3)_3MN_3 \xrightarrow[10^{-2}\ \text{mbar}]{} N_2 + ? \qquad (1)$$

$$M = Si, Ge$$

In addition, and in order to correctly interpret experimental data, we carried out a theoretical analysis of the various possibilities of molecular rearrangement and then calculated the ionization potentials of the compounds that could have formed.

Theoretical Study of Rearrangement Mechanisms

Before the experimental data obtained by flash pyrolysis of $(CH_3)_3MN_3$ (M = Si, Ge) and the resulting conclusions are reported we will present the different rearrangement reactions the silicon compound can undergo after the loss of a nitrogen molecule. In the theoretical part, all the energy calculations of various intermediates and reaction products included a complete optimization of geometric parameters at the SCF level. We used the Monstergauss program with a 3.21G* basis set (see computational details). Thus, instead of the trimethylated compounds, we considered the monomethylated derivatives for the obvious reason of calculation times. Tests performed in ab initio on several examples and on all the compounds in MNDO,[31] a semiempirical method also including geometry optimization, showed that the qualitative order of stability between the trimethylated molecules and their models was identical, with quantitative results very close. Nevertheless, we note that the calculated energies are only given as semiquantitative indications because they depend upon the quality of the calculations and, in particular, on the basis sets. This can be important for the molecules close in energy (~10 kJ·mol^{-1}).

We considered three rearrangement mechanisms differing at the level of metastable intermediates but which were capable of yielding identical products. We will not present two other theoretically possible mechanisms leading to a silyl nitrile, $(CH_3)_2HSiC{\equiv}N$, or to a silylene, $CH_3SiN(CH_3)_2$, which could polymerize or react with another molecule. In all cases, the predicted photoelectron spectra of these products were not the same as those obtained after flash pyrolysis.

I. Reaction with a Silanimine Intermediate (Curtius Reaction). In the special case of the nonsubstituted silyl azide H_3SiN_3, this is the only mechanism possible. Thus, Cradock et al.[14] observed the silaisonitrile, Si≡NH, at low temperature after a flash photolysis reaction (eq 2).

$$H_3SiN_3 \xrightarrow{h\nu} [H_2Si{=}NH + N_2] \rightarrow Si{\equiv}NH + H_2 + N_2 \qquad (2)$$

This Curtius reaction may be compared to those occurring in the photochemical fragmentation of $(CH_3)_3SiCHN_2$[32,33] and of H_3CN_3[34,36] (eq 3 and 4) or in the thermal dissociation of H_3CN_3[37] (eq 5). In our case, this mechanism is a two-step reaction (eq 6) which is modeled in the calculations by reaction 7.

$$(CH_3)_3SiCHN_2 \xrightarrow{h\nu} (CH_3)_2Si{=}CHCH_3 + (CH_3)_3SiCH + N_2 \qquad (3)$$

$$H_3CN_3 \xrightarrow{h\nu} H_2C{=}NH + C{\equiv}NH + H_2 + N_2 \qquad (4)$$

$$H_3CN_3 \xrightarrow[-N_2]{>800\ K} H_2C{=}NH \xrightarrow[-H_2]{>850\ K} HCN \qquad (5)$$

$$(CH_3)_3SiN_3 \rightarrow (CH_3)_2Si{=}NCH_3 + N_2 \rightarrow Si{\equiv}NCH_3 + C_2H_6 + N_2 \qquad (6)$$

$$H_2(CH_3)SiN_3 \rightarrow H_2Si{=}NCH_3 + N_2 \rightarrow Si{\equiv}NCH_3 + H_2 + N_2 \qquad (7)$$

(a) First Step: Formation of Silanimine. Silanimines, $R_2Si{=}NR'$, had long been considered as merely a reaction intermediate after photolysis[26-28,38,39] or gas-phase pyrolysis.[2,19,40] One has recently been isolated by crystallization from a pentane solution at 195 K[41] (R = t-Bu, R' = Si(t-Bu)$_3$). In parallel to our work, a theoretical study was carried out in double-ζ quality basis set[42] on a simple silanimine, H_2SiNH, which, in comparison to our calcu-

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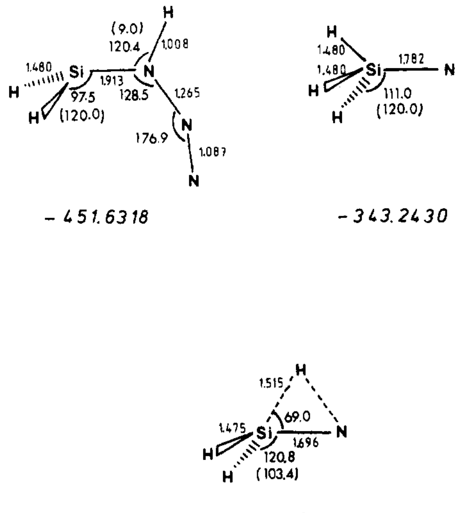

Figure 2. Calculated (3.21G*) structures (Å, d^0) and total energies (hartree) of the minima (H_2SiNHN_2, H_3SiN) and the saddle point ($H_2\overline{Si-H-N}$) lying between H_3SiN and H_2SiNH. The values in parentheses are the values of the dihedral angles defined by the bond and the page plane.

lations, takes the p polarization orbitals on the hydrogen atoms into account. The results were very close to ours (Figure 1), thereby confirming the validity of our approach (see calculation methods). This validity was also supported by two very recent theoretical studies. In the first,[43] the authors used a 6–31G* basis set including the electronic correlation (fourth-order Møller–Plesset calculations) of a large series of compounds including H_2SiNH and SiNH. In the second,[44] the structure of silanimine was predicted on the basis of multiconfigurational SCF calculations.

These results reflect a pronounced polarity of the Si=N double bond (net charges of +0.62e on Si and −0.64e on C) and a reactivity which is undoubtedly high. As in the case of silane- and germanethiones and germanones,[16–18] the two highest occupied molecular orbitals (HOMO) are relatively high in the monomethylated model (SCF energies are, respectively, −9.85 eV for the $n_N{}^\sigma$ type orbital and −9.35 eV for the π_{SiN} orbital) and localized primarily on the nitrogen atom.

The formation of a nitrene intermediate in the reaction leading to a silanimine is controversial. In a first approach, we analyzed the MNDO potential energy hypersurface of the singlet ground state of the H_3SiN_3 system. A saddle point search algorithm[45,46] was used in these calculations, enabling us to find the lowest saddle point on the pathway between two minima on the potential energy hypersurface. In a second approach we have calculated the stationary points (Figure 2) by using an SCF ab initio (3.21G*) method. These points have been checked by the evaluation of the force constant matrix.

There are two possible pathways. The first corresponds to a concerted reaction and passes through a metastable intermediate, H_2SiNHN_2. In this pathway, the first barrier is associated to the migration of a hydrogen from the silicon toward the nitrogen, the second one coming from the loss of N_2. The second pathway requires the formation of a singlet nitrene.[47] In contrast to the MNDO results that indicated a higher stability for H_2SiNHN_2 vs. H_3SiN + N_2, the ab initio calculations give a nitrene + N_2 energy lower than that of H_2SiNHN_2 (97.86 kJ·mol^{-1}). Thus these ab initio results (Figure 2) show that the more favorable pathway is that which involves the formation of the silyl nitrene, especially as the differences between the activation energies between H_3SiN and H_2SiNH are relatively low (1.52 kJ·mol^{-1} above the nitrene).

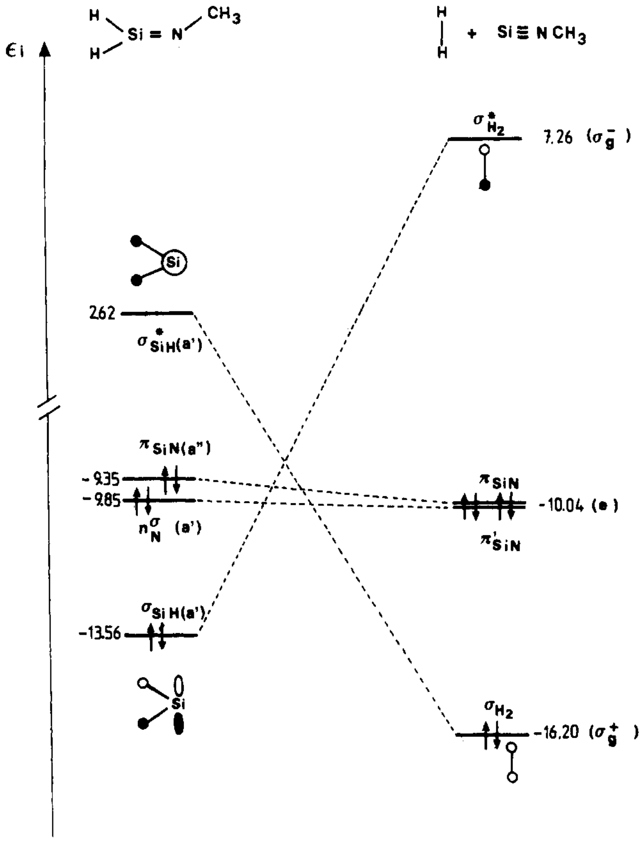

Figure 3. Correlation diagram (3.21G*) between the frontier orbitals of the silanimine and the system silaisonitrile + H_2.

(b) Second Step: Formation of Silaisonitrile. As early as 1966, Ogilvie and Cradock[14] isolated silaisonitrile at 4 K (argon matrix) after photolysis of H_3SiN_3. They then showed that this molecule and its germanium analogue are linear.[53] Several theoretical studies have been devoted to the higher stability of the silaisonitrile in comparison to its HSi≡N isomer.[43,54–57] These authors esti-

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(47) This state is in fact less stable than the triplet which is a general property of both nitrenes[48–50] and carbenes. It is nonetheless admitted that only singlet ground states should be considered in practice in azide pyrolysis as result of spin conservation. Rearrangement products of triplet nitrene are minor.[51,52]

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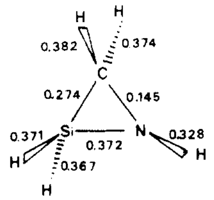


Figure 4. Mulliken population (3.21G*) of silaaziridine.

mated the stability difference to be between 230 and 290 kJ·mol^{-1} and predicted a barrier of about 40 kJ between the two isomers. These results were recently confirmed by the synthesis of phenyl silaisonitrile using experimental conditions similar to ours.[19]

In our case, the silaisonitrile in principle can be obtained from the silanimine only at high temperature. The activation barrier is very high since silanimine dissociation requires a forbidden crossing between an occupied orbital and a virtual orbital. This crossing is shown schematically in Figure 3 for our reaction $H_2Si{=}NCH_3 \rightarrow Si{\equiv}NCH_3 + H_2$.

We will return to the electronic structure of the silaisonitrile and that of its germanium homologue in the last part of this work.

According to our calculations, this model reaction is very slightly endothermic (ΔH = 4.9 kJ·mol^{-1}). This very low value, however, does not enable us to establish an unequivocal conclusion on the sign of ΔH in the actual reaction.

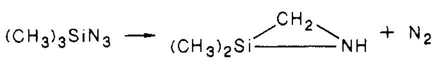
II. Reaction with a Silanitrile Intermediate. This reaction (eq 8) leads to the same compounds as the preceding reaction but formally passes through the silanitrile discussed in the above section. It is similar to that described by Bock and Dammel[19] for the pyrolysis of $C_6H_5Si(N_3)_3$ (eq 9). This type of reaction, nevertheless,

$$(CH_3)_3SiN_3 \rightarrow CH_3Si{\equiv}N + C_2H_6 + N_2 \rightarrow Si{\equiv}NCH_3 + C_2H_6 + N_2 \quad (8)$$

$$C_6H_5Si(N_3)_3 \xrightarrow{>1000\ K} Si{\equiv}NC_6H_5 + 4N_2 \quad (9)$$

requires a very high-temperature because of the low stability of the methylsilanitrile which, on the basis of our 3-21G* calculations, is 280 kJ·mol^{-1} above methylsilaisonitrile. It is thus reasonable to consider that the Curtius reaction is energetically preferable.

III. Reaction with a Silaaziridine Intermediate. After the loss of a nitrogen molecule, the pyrolysis of trimethylsilyl azide may lead to the formation of a silaaziridine intermediate in the first step (eq 10) or in our model system (eq 11).



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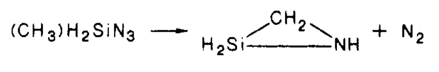


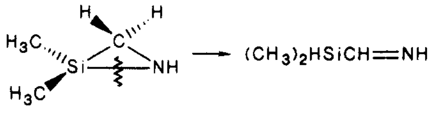
(11)

This ring is relatively stable, since its energy (−382.1693 hartree) is 38.5 kJ·mol^{-1} lower than that of the N-methylated silanimine $H_2Si{=}NCH_3$ and 43.2 kJ·mol^{-1} lower than that of the $Si{\equiv}NCH_3 + H_2$ system. It may rearrange by opening one of the three bonds and by 1,2-migration of a hydrogen or a methyl group, furnishing different products. The Mulliken populations associated with the ring bonds (Figure 4) enable us to determine the binding forces and thus their relative ease of rupture. Thus, the strongest bond is Si–N while the Si–C bond is much more fragile. Finally, the C–N bond, in principle, should require the lease energy to break in light of these populations.

These Mulliken populations associated with binding strength can be qualitatively correlated with the activation barriers. So the break of the strongest bond should correspond to the highest activation energy. If we consider that the heat of pyrolysis is sufficient for passing over these barriers, we must look at the thermodynamical aspect, i.e., the total energy of different products.

We successively consider the three possibilities for the ring opening, noting the relative energy (in kJ·mol^{-1}) of each product in comparison to that of the silaaziridine.

(a) Reorganization by Breaking the Si–N Bond. When the ring opens via the Si–N bond, simultaneously with the migration of a ring carbon-bound hydrogen into the Si, the resulting structure is a *C*-silyl imine (eq 12) or, according to the model (eq 13). This imine is relatively



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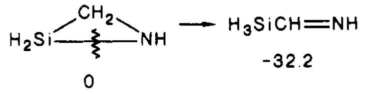
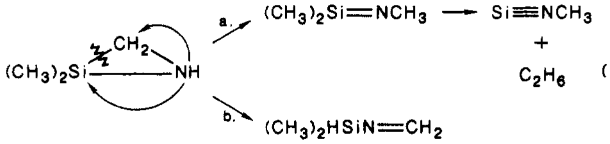


(13)

stable (−382.1815 hartree), since it is 32.2 kJ·mol^{-1} lower in energy than that of silaaziridine.

(b) Reorganization by Breaking the Si–C Bond. When the ring opens by scission of the Si–C bond, in principle less difficult than the above reaction, different products are formed, depending on whether the nitrogen-bound hydrogen migrates to carbon or to silicon (eq 14) or according to our calculations (eq 15). We will not return to reaction a, whose second step is similar to the Curtius reaction already considered.



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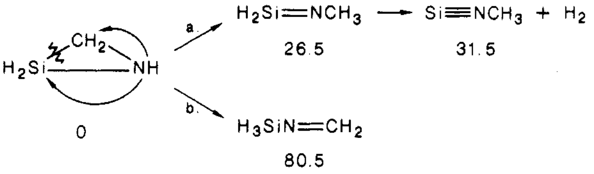
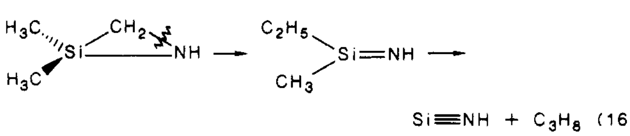


(15)

Reaction b again generates an imine, but N-silylated this time. This imine is the most stable (−382.2000 hartree) of all the products considered for these various molecular reorganizations. Its total energy is 48.5 kJ·mol^{-1} lower than that of its *C*-silyl homologue, i.e., 89.6 kJ·mol^{-1} more stable than the silaaziridine, the starting point for the reaction.

(c) Reorganization by Scission of the C–N Bond. Breaking this bond, in principle, the weakest of the three, followed by a 1,2-migration of a methyl group, leads to a silanimine that may subsequently yield an silaisonitrile (eq 16 and 17). The products of this reaction are much more



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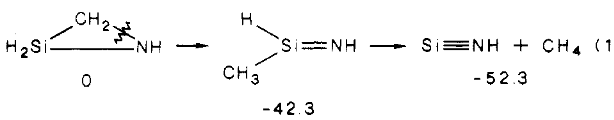

(17)

stable than their N-methylated homologues. Furthermore,

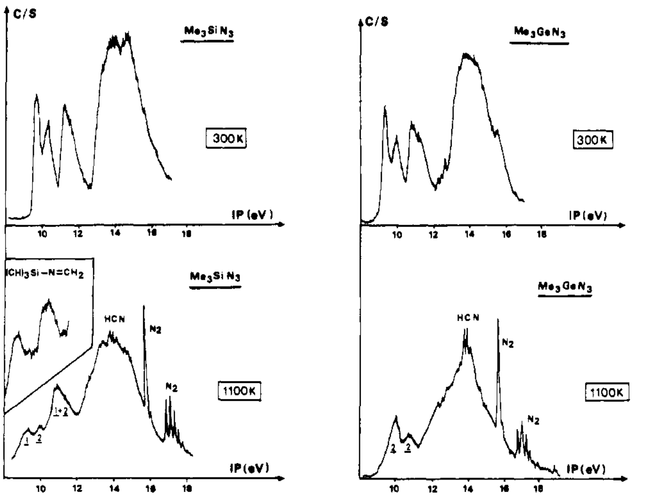

Figure 5. He I photoelectron spectra of trimethylsilyl azide and trimethylgermyl azide before (300 K) and after (1100 K) flash pyrolysis.

Table I. Vertical Ionization Potentials (eV) of Trimethylsilyl Azide and Trimethylgermyl Azide before (300 K) and after (1100 K) Flash Pyrolysis

$(CH_3)_3SiN_3$	300 K	9.6	10.2	11.15	11.4
	1100 K	9.3	9.9	10.9	
$(CH_3)_3GeN_3$	300 K	9.3	10.0	10.8	11.2
	1100 K	9.8	10.7		

the final product is SiNH, a compound known and isolated at low temperature.[14]

After this theoretical analysis of the various possible molecular rearrangements of trimethylsilyl azide that could occur after the loss of nitrogen, we may conclude that, when we consider the thermodynamic stability of the products, the probabilities of obtaining the compounds are in the following order: $(CH_3)_2HSiN{=}CH_2 > Si{\equiv}NH > (CH_3)_2HSiCH{=}NH \gg Si{\equiv}NCH_3$.

This conclusion is in agreement with the results of cold (10 K) photolysis of the same precursor, which apparently yields one of the two imines considered as the sole product,[58] probably the more stable *N*-silyl imine.

Experimental Study of the Flash Pyrolysis of $(CH_3)_3SiN_3$ and $(CH_3)_3GeN_3$

Figure 5 shows the photoelectron spectra of the two precursors $(CH_3)_3SiN_3$ and $(CH_3)_3GeN_3$, recorded at ambient temperature (300 K) and also after undergoing a flash pyrolysis at 1100 K (10^{-2} mbar). The shape of the spectra is considerably changed at this temperature, with the appearance of nitrogen peaks. Table I lists the ionization potential values determined for these temperatures, where there is a clear difference between the silicon derivative and its germanium homologue. For a similar structure, the latter should present slightly lower first ionization potentials, which is what is seen with the precursors (spectra at 300 K). After pyrolysis, however, the first band of the germanium derivative exhibits a maximum at 9.8 eV while that of the silicon homologue is at 9.3 eV. On the other hand, this band of the germanium compound is to be compared to the second band of the silicon analogue at 9.9 eV. It thus appears a priori that pyrolysis of the silyl azide leads to two distinct compounds while that of the germyl azide yields only one.

We may compare these experimental data (Table I) to calculations performed on the different silicon compounds discussed in the theoretical part of this work (Table II). First, it is evident from these values that we do not detect trimethylsilanimine, whose first ionization potentials certainly are lower than the experimental value of 9.3 eV. However, this value and that associated with the third band (10.9 eV) may correspond to the *N*-silyl imine $(CH_3)_2HSiNCH_2$ (note 1 in Figure 5). This is supported by the photoelectron spectrum of the trimethyl homologue $(CH_3)_3SiNCH_2$, obtained in the laboratory[60] by a dehydrocyanation reaction on a solid support of the corresponding precursor. Not only do the two spectra have a similar profile (the second band is much more intense than the first), but also the ionization potential values are in agreement, given the expected effect of an additional methyl group: 9.15 and 10.65 eV for the trimethylsilanimine.

Table II. Calculated Ionization Potentials (eV) of Trimethylsilyl azide and Several Possible Pyrolysis Products with Perturbational Corrections (IP_{calcd}; See Computational Details) after SCF ab Initio (4.31G*) Calculations

$(CH_3)_3SiN_3$	IP_{calcd}	10.07	10.60	11.77	11.87
	IP_{exptl}	9.6	10.2	11.15	11.4
SiNH	IP_{calcd}	10.28	10.28	11.58	18.05
	IP_{exptl}	9.9	9.9	10.9	
$SiNCH_3$	IP_{calcd}	9.62	9.62	11.25	15.08
$(CH_3)_2HSiNCH_2$	IP_{calcd}	9.33	11.16	12.02	12.50
	IP_{exptl}	9.3	10.9		
$(CH_3)_2HSiCHNH$	IP_{calcd}	10.04	11.38	12.28	12.50
$(CH_3)_2SiNCH_3$	IP_{calcd}	8.10	8.21	12.05	13.41

Table III. Calculated Energies E_T (PSHONDO Method) of Silyl (Germyl) Imine and Sila (Germa) Nitrile

	$H_3SiN{=}CH_2$	$Si{\equiv}NH + CH_4$	$H_3GeN{=}CH_2$	$Ge{\equiv}NH + CH_4$
total energy E_T, hartree	−21.8053	−21.7997	−21.6605	−21.6653
ΔE_T, kJ·mol^{-1}	0	14.7	0	−12.6

As the stated above, the first two bands (9.8 and 10.7 eV) of the PE spectrum of the $(CH_3)_3GeN_3$ pyrolysis products are to be compared to the second (9.9 eV) and the third (10.9 eV) bands of the $(CH_3)_3SiN_3$ pyrolysis products (this third band is thus associated with two different compounds). On the basis of the value of these potentials and, above all, the relative intensity of the bands (the first band is about 2 times more intense than the second), we can attribute these spectra to germaisonitrile, GeNH, and to silaisonitrile, SiNH (note 2 in Figure 5). The first band is associated with a degenerate state with π symmetry.

Finally, the broad band beyond 11.5 eV arises not only from the higher energy bands of compounds 1 and 2 but also from the propane formed with the metalla nitrile analogues.

In order to confirm this interpretation and to explain the different behavior of the silicon and germanium derivatives, we carried out PSHONDO calculations (4-31G*) on the four compounds $SiNH(+ CH_4)$, $GeNH(+ CH_4)$, H_3SiNCH_2, and H_3GeNCH_3, optimizing the SiN and GeN bonds point by point. (We were unable to use the MONSTER-GAUSS program for these calculations since we did not have the theoretical values of the 3–21* basis set for germanium.)

The energy values shown in Table III reflect a difference in behavior: the *N*-silyl imine is more stable than the iminosilylene, while the reverse order is observed for the

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Table IV. Calculated Ionization Potentials IP_{calcd} (eV) (CI Level) Compared with the Experimental Values of Silaisonitrile and Germaisonitrile

SiNH	IP_{calcd}	10.18 ($^2\Pi$)	10.18 ($^2\Pi$)	10.71 ($^2\Sigma^+$)
	IP_{exptl}	9.9	9.9	10.7
GeNH	IP_{calcd}	9.85 ($^2\Pi$)	9.85 ($^2\Pi$)	10.90 ($^2\Sigma^+$)
	IP_{exptl}	9.8	9.8	10.7

germanium compounds. This result is to be compared to the conclusion of Preuss et al. on the relative energies of HAB systems.[56] For MNH type compounds (M = C, Si, Ge), it thus seems that stability follows the order of the periodic table. The higher stability of the germanium compound is probably related to a slightly greater overlap population for Ge–N (0.76) than for Si–N (0.69) and thus to a slightly stronger and slightly less polarized bond (the net charge calculated for germanium is 0.37e while it is 0.41e for silicon; inversely, they are −0.65e and −0.69e, respectively, for the nitrogen atoms of GeNH and SiNH).

We wished to support our conclusion on the formation of silaisonitrile and germaisonitrile in the pyrolysis of the azides by carrying out a more rigorous calculation of their first ionization potentials (CIPSI program, see calculation methods). The theoretical values are compared to the experimental values in Table IV. For the silicon derivative, they correspond to bands 2 and 3 and for the germanium derivative to bands 1 and 2 (Figure 5). It should be noted that, as expected, the first two potentials associated with the first two degenerate ionic states ($^2\Pi$) are slightly lower for GeNH than for SiNH. They correspond to π-type orbitals of $M{\equiv}N$ bonds. Furthermore, for $Si{\equiv}NH$, the experimental value of the first potential (9.9 eV) is identical with that determined by Bock et al.[19] in the case of $Si{\equiv}NC_6H_5$ for the potential associated with the same π_{SiN} orbital.

The third potential, on the other hand, is slightly higher for the germanium compound than for the silicon analogue. This arises from the fact that the corresponding doublet state ($2\Sigma^+$) is constructed primarily from the 3s (or 4s) atomic orbitals, which is consistent with the order of the ionization potentials of the Si and Ge atoms,[61] 13.46 eV for 3s (Si) and 14.3 eV for 4s (Ge), and may also be related to the greater stability of GeNH.

Conclusion

The theoretical analysis of the gas-phase thermal fragmentation of trimethylsilyl azide and trimethylgermyl azide, combined with calculations of the ionization potentials of the rearrangement products, has led to the following conclusions on the nature of the thermolysis products.

$$(CH_3)_3SiN_3 \xrightarrow[1100\ K,\ 10^{-2}\ mbar]{} \underset{1}{(CH_3)_2HSiN{=}CH_2} + N_2 + \underset{2}{Si{\equiv}NH}$$

$$(CH_3)_2GeN_3 \xrightarrow[1100\ K,\ 10^{-2}\ mbar]{} \underset{2}{Ge{\equiv}NH} + N_2$$

In our experimental conditions, we observed silaisonitrile and the N-silylated imine in equimolar proportions. For the germanium derivarive, on the other hand, we observed only the germaisonitrile. This difference most probably is due to the greater stability of GeNH in comparison to that of SiNH.

Experimental and Computational Details

The He I photoelectron spectra were recorded on a PE spectrometer 0078 of "Photoelectron Laboratories LTD" with argon and xenon used as internal calibrants (12.126 and 13.443 eV for $^2P_{1/2}$ and $^2P_{3/2}$ of Xe; 15.755 and 15.93 eV for $^2P_{1/2}$ and $^2P_{3/2}$ of Ar). Flash pyrolysis was carried out with a "variable-temperature probe"[62] allowing us to heat the vapor above 1300 K in a ceramic tube during a few tenths of seconds. The short pathway distance of about 5 cm between the end of the heating zone and the target chamber of the PE spectrometer allows the recording of photoelectron spectra of transient compounds (ca. 0.1 s) or rearrangement derivatives.

The molecular geometries were fully optimized with respect to all structural parameters (bond lengths and angles) by the Broyden–Fletcher–Goldfard–Shanno gradient method[63] included in the MONTERGAUSS program.[64] The split valence 3.21G basis set[65,66] was used, augmented by one set of d polarization functions on silicon and nitrogen. Several tests have shown the results were little influenced by polarization functions on carbon and hydrogen.

The experimental ionization potentials were compared to the theoretical values calculated by the PS HONDO program,[67,68] a variant of the HONDO[69] program in which pseudopotentials are included in the SCF level. Polarization and correlation orbitals effects were approximated by using a procedure based on a partial perturbative treatment.[70] The pseudopotentials were taken from Hartree–Fock double-ζ atomic calculations of Clementi and Roetti.[61] The basis set was of the 4.31G type with d polarization orbitals on silicium, germanium, and nitrogen.

For SiNH and GeNH, we performed a rigourous calculation of first ionization potentials by means of a program[72] using the CIPSI algorithm[73] (CI calculations on the ground states and the first ionic states). A variational zeroth-order wave function was built in an iterative selection of the most important single and double excited determinants formed from the former reference subspace, the other ones being taken into account through a second-order Møller–Plesset perturbation. The reference subspace contained between 30 and 60 determinants. The number of determinants taken into account in the perturbative treatment was between 3 × 10^5 and 9 × 10^5.

Acknowledgment. We thank Drs. A. Baceiredo and G. Bertrand (Toulouse, France) for gifts of azides samples and Dr. J. M. Denis for a gift of the precursor of $(CH_3)_3SiNCH_2$. The calculations have been performed in part on the Cray-One of "Centre Vectoriel pour la recherche", Ecole Polytechnique (ATP Cray 1985) and, in part, on the Cray-One of the "Societê Nationale Elf Aquitaine-Production".

Registry No. $(CH_3)_3SiN_3$, 4648-54-8; $(CH_3)_3GeN_3$, 7514-84-3.

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