Spectroscopic Studies of the Photodecomposition of Silyl Azides in Argon Matrices near 4°K: Detection of Iminosilicon, HNSi

By J. F. OGILVIE
(*Department of Physical Chemistry*)
and S. CRADOCK
(*Department of Organic and Inorganic Chemistry, University of Cambridge, Lensfield Road, Cambridge*)

THE infrared absorption spectra of silyl and trideuterosilyl azides and their photodecomposition products in solid argon matrices near 4°K have been investigated, using techniques similar to those employed in comparable studies of diazomethane.[1] The infrared spectra were recorded on a Unicam SP100 spectrophotometer with KBr prism and two gratings, scanning from 370 to 3650 cm.$^{-1}$; a multilayer transmission filter of tellurium and thallous chloride reduced stray light in the KBr range to an amount undetectable at 375 cm.$^{-1}$

After irradiation of SiH_3N_3 and SiD_3N_3 separately in argon (matrix ratio of 300) near 4°K by means of a Philips HPK 125w high-pressure mercury lamp, infrared absorption spectra showed a decrease of intensity of bands assigned to silyl azides,[2] and the appearance of several new bands. The most notable of these are listed in the first two columns of the Table. The most suggestive of these frequencies is 3583 cm.$^{-1}$, coincident with that previously assigned to the N–H stretching frequency of hydrogen isocyanide, HNC, produced after irradiation of methyl azide in an argon matrix.[3] The smallest frequency in each of these columns is also similar to the corresponding bending frequency of either HNC or DNC.[3] If one assumes that the frequencies of the first column belong to the linear molecule HNSi with bond lengths as listed, the frequencies for DNSi can be calculated, as in the third column. There is good agreement of computed and observed frequencies. For ν_1 of DNSi, a frequency 2649 cm.$^{-1}$ can be calculated from the FG-matrix method with the usual high-frequency approximation,[4] and a correction for anharmonicity previously found successful for triatomic radicals.[5] In the Table are also stated the force constants, calculated from the equations given by Herzberg,[6] and Milligan's data[3] pertaining to HNC and DNC for comparison.

TABLE. *Proposed fundamental frequencies, force constants, and dimensions of* HNSi *and* DNSi, *compared with similar data for* HNC *and* DNC.[3]

	Units	HNSi	DNSi	DNSi (calc.)	HNC	DNC	DNC (calc.)
ν_1	cm.$^{-1}$	3583	2669	2674	3583	2733	2704
ν_2	cm.$^{-1}$	523	395	402·5	535	413	421
ν_3	cm.$^{-1}$	1198	1166	1162	2032	1940	1940
k_1	10^5dyne cm.$^{-1}$	7·71			6·95		
k_2	10^5dyne cm.$^{-1}$	8·72			16·47		
k_δ	10^{-11}dyne cm.	0·136			0·131		
r_1	Å	1·005			1·01		
r_2	Å	$\sim$1·54			1·17		
angle	degrees	180			180		

The force constants k_1 of HNC and HNSi are similar; the significant difference is the result of a correction of the observed HNSi and DNSi frequencies for anharmonicity. The value of k_2 for HNSi is much smaller than for HNC, but is similar to the value for NSi itself, 8·3734, and much smaller than the force constant 28·8 which can be calculated for the isocyanide CNN for which the CN stretching frequency 2847 cm.$^{-1}$ was observed.[7] k_δ for HNSi is slightly larger than for HNC, but the bond length of 1·54 Å required to yield the ν_2 frequency is in excellent agreement with the bond length of N–Si, 1·572 Å. The difference in the latter bond lengths is entirely consistent with the larger k_2 force constant of HNSi. The Si–N bond lengths of HNSi and NSi are both much less than the usual value of 1·70 Å for SiN single bonds, but this phenomenon of bond length shrinkage is generally associated with multiple bonding.[8]

Such a large force constant k_2 certainly indicates a ground state of singlet multiplicity for iminosilicon, and the small force constant k_δ is entirely consistent with a collinear nuclear equilibrium configuration.

Iminosilicon represents the first detected discrete stable molecule with silicon multiply bonded to another atom, with the exception of transient diatomic free radicals.

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