The Reactions of Some Silylamines with Carbon Dioxide and Related Molecules

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Trisilylamine and *N*-methyldisilylamine do not react with carbon dioxide, carbon disulphide, or carbon oxysulphide at up to 100° and pressures up to 30 atmospheres. *NN*-Dimethylsilylamine combines with carbon dioxide to give silyl *NN*-dimethylcarbamate, and with carbon disulphide to give silyl *NN*-dimethyldithiocarbamate; with carbon oxysulphide, a compound is produced, formulated as *O*-silyl *NN*-dimethylmonothiocarbamate, whose n.m.r. spectrum indicates that rotation about the $Me_2N{-}C$ bond is restricted.

THE addition of amino-derivatives of non-metals or of metalloids to unsaturated systems has been widely studied. Breederveld [1] found that *NN*-diethyltrimethylsilylamine forms 1 : 1 addition compounds with carbon dioxide and with carbon disulphide, and he formulated the products as derivatives of carbamic acid. Since then, the addition of amino-derivatives of germanium,[2] tin,[3] boron,[4] phosphorus,[5] arsenic,[6] and sulphur [7] to similar unsaturated systems has been reported. In all these investigations, organo-substituted derivatives of the elements concerned were used; we have studied the reactions between carbon dioxide, carbon disulphide, and carbon oxysulphide and three amines containing the SiH_3 group. The presence of this group has made it particularly convenient to study the systems by proton n.m.r. spectroscopy at room temperature and below, using changes in chemical shift and in ^{29}SiH coupling constants to indicate reaction; the sensitivity of the n.m.r. parameters of the silylamines to changes in temperature and solvent will be reported elsewhere.[8] From these and other physical and chemical data, we have made some deductions about the nature of the products.

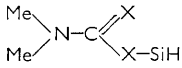
We found no evidence that either trisilylamine or *N*-methyldisilylamine reacts with CO_2, CS_2, or COS, when sealed in n.m.r. tubes at pressures of at least 30 atm., either on prolonged standing at room temperature or on heating to 100° for short periods, except in one tube containing CO_2 and $MeN(SiH_3)_2$, and, since the experiment could not be repeated, we attribute the results to the presence of traces of impurity. In some of the systems containing $MeN(SiH_3)_2$, changes in the n.m.r. spectrum during prolonged standing at room temperature are consistent with the formation of Si–N polymers or ring compounds through SiH migration:

$$n(SiH_3)_2NMe = (MeNSiH_2)_n + nSiH_4$$

In contrast to this behaviour, *NN*-dimethylsilylamine gave equimolar addition compounds with CO_2, CS_2, and COS, reaction occurring most readily with CO_2. With CS_2, the product was a white solid, involatile at room temperature, which sublimed with some decomposition *in vacuo* at 100°. When CO_2 and *NN*-dimethylsilylamine were allowed to react at room temperature, some monosilane was always recovered from among the volatile products; the residue was a colourless, viscous liquid, which deposited a white solid when allowed to stand at room temperature, with evolution of a total quantity of monosilane approximately corresponding to all the Si–H bonds present in the amine originally taken. Experiments with $SiD_3{\cdot}NMe_2$ showed that all the monosilane was formed from SiH hydrogen. Reaction of the amine with CO_2 at −35° did not initially lead to the formation of monosilane, which was thus produced in the decomposition of the adduct, rather than by the decomposition of the reacting amine before reaction. The adduct of *NN*-dimethylsilylamine with COS was also unstable at room temperature, evolving monosilane, but small amounts appeared to sublime unchanged during 24 hr. *in vacuo*.

Though all the adducts are more-or-less unstable at room temperature in the absence of solvent, they are much more stable when dissolved in carbon tetrachloride. The ultraviolet, infrared, and n.m.r. spectra of the three compounds were obtained in this solvent; the solutions could be supercooled without difficulty to at least −30°, so that n.m.r. spectra could be obtained of systems 50° below room temperature.

The infrared, ultraviolet, and n.m.r. spectra of the adducts formed from CO_2 and CS_2 are all consistent with the formulation of these compounds as silyl *NN*-dimethylcarbamate (I; X = O) and silyl *NN*-dimethyldithiocarbamate (I; X = S), respectively.

(I) 

The infrared spectrum of the carbamate contains a strong peak in the region associated with C=O stretching, and the infrared spectrum of the dithiocarbamate is very like the spectra of *NN*-dialkyldithiocarbamates.[9] The SiH chemical shifts and ^{29}SiH coupling constants are also in the range associated with SiH_3O systems (for the carbamate) and SiH_3S systems (for the dithio-

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carbamate) (see Table 1), in the spectra of samples prepared from 95%-labelled $SiH_3{}^{15}NMe_2$; $^{15}NSiH$ coupling was not observed in the SiH resonance. The CH resonance, identified by intensity, by ^{13}CH satellites, and by ^{15}NCH coupling, is found in the spectrum of the carbamate about 0·4 p.p.m. to low field of its position in the parent amine, and is still further to low field in the spectrum of the dithiocarbamate. In the spectra of the ^{14}N adducts, the *N*-methyl protons give rise to single resonances, even at temperatures close to −40°. If rotation about the $Me_2N–C$ bonds were substantially restricted, two methyl proton resonances would be expected, unless some other process or property led to equivalence of the *N*-methyl groups. In the n.m.r. spectrum of methyl *NN*-dimethylcarbamate dissolved in carbon tetrachloride, the *N*-methyl protons give rise to a single resonance at room temperature, but the *N*-methyl proton resonance of methyl *NN*-dimethyldithiocarbamate in the same solvent is very broad, and it splits just below room temperature into two peaks of equal intensity, showing that under these conditions rotation about the $Me_2N–C$ bond is restricted.[14] If, therefore, the methyl proton resonances of both silyl *NN*-dimethylcarbamate and silyl *NN*-dimethyldithiocarbamate are collapsed through rapid rotation even at −40°, the barriers to rotation about the $Me_2N–C$ bond in the silyl and the methyl esters of *NN*-dimethyldithiocarbamic acid must be substantially different. If, on the other hand, the $-C(X){\cdot}X{\cdot}SiH_3$ groups are in the planar *cis* configuration, as has been suggested for other silyl esters,[15] the effective chemical shift between the two methyl groups might be very small; moreover, rapid intramolecular exchange of SiH_3 groups between the two X atoms could render the methyl groups equivalent. Such exchange is possible, but there is no other evidence to indicate that it occurs.

TABLE 1

Proton chemical shifts in some compounds containing SiH_3O or SiH_3S groups

Compound	$\tau(SiH_3)$ (p.p.m.)	Compound	$\tau(SiH_3)$ (p.p.m.)
$(SiH_3)_2O$	5·39 [a]	$CH_3CO_2SiH_3$	5·53 [c]
$SiH_3{\cdot}OCH_3$	5·51 [b]	$CF_3CO_2SiH_3$	5·32 [c]
$(SiH_3O)_2SiH_2$	5·33 [b]		
$(SiH_3O)_3SiH$	5·34 [b]	$(SiH_3)_2S$	5·64 [a]
HCO_2SiH_3	5·45 [c]	$SiH_3{\cdot}SCF_3$	5·58 [d]

[a] Ref. 10. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13.

It is more difficult to establish the structure of the compound formed with COS. In principle, addition could take place across either the C=O or the C=S bonds. The single SiH resonance, taken with the single set of ^{29}SiH satellites, strongly suggests that the product is a single compound. In the infrared spectrum there is only a weak band in the region associated with C=O stretching, but there is a very strong band near 1500 cm.$^{-1}$ (where a strong band, assigned to a stretching mode of the heavy-atom skeleton, is observed in the spectra of *NN*-dialkyldithiocarbamates [9]). This implies that addition has occurred across the C=O bond, giving *O*-silyl *NN*-dimethylmonothiocarbamate, and this implication is supported by a consideration of the n.m.r. chemical shifts. The value of τ (SiH), though less than in the carbamate or the dithiocarbamate, is much closer to τ (SiH) in other SiH_3O compounds than to typical values of τ (SiH) in SiH_3S systems (see Table 1). Similarly, the methyl proton chemical shifts, likely to be sensitive to the nature of the C=X bond, are closer to those found for the dithiocarbamate than to those found for the carbamate. Moreover, rough calculations based on bond energies [16] suggest that the SiH_3O derivative is the more likely to be formed.

The only surprising feature of the spectrum is that the *N*-methyl resonance is split into two components of equal intensity, separated by 0·12 p.p.m.; both components must be due to *N*-methyl protons, for both show approximately equal splitting by ^{15}N in the spectrum of a sample prepared from $SiH_3{\cdot}{}^{15}NMe_2$. The splitting of the main resonance could arise directly from restriction of rotation about the $Me_2N–C$ bond; indeed, without restriction of rotation it is hard to see how any such non-equivalence could arise. There was, however, no sign of collapse in the splitting even at *ca.* +60°, whereas in the spectra of the other two compounds no splitting was detected at *ca.* −40°. Perhaps the barrier to rotation is much greater in the derivative of COS than in the carbamate or the dithiocarbamate. If, on the other hand, exchange of SiH_3 groups is responsible for the equivalence of the methyl groups in the two last-named compounds, it is easy to see why the splitting is observed in the spectrum of the adduct of COS; such exchange could not lead to equivalence of the methyl groups in that compound unless rotation about the $Me_2N–C$ bond were rapid.

EXPERIMENTAL

Reactions of Trisilylamine.—Trisilylamine was sealed in 5 mm. o.d. Pyrex n.m.r. tubing with enough CO_2 to give a pressure of at least 30 atm. at room temperature. No change in the n.m.r. parameters of the amine was observed after the tube had been kept at room temperature for several days, or after heating it to 100° (3 hr.). There was no sign of reaction when trisilylamine was treated similarly with COS, or when the amine was heated with an excess of CS_2.

Reactions of N-*Methyldisilylamine.*—Many tubes were

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made up containing CO_2, CS_2, or COS mixed with *N*-methyldisilylamine in varying proportions. In one tube containing the amine and CO_2, changes in the n.m.r. spectrum were observed that were consistent with reaction. Since all attempts to repeat this reaction failed, we conclude that the additional peaks in the n.m.r. spectrum may have arisen from the presence of traces of water in the sample of CO_2. Even after standing at room temperature for several days, the spectra of the material in the other tubes corresponded with that of the starting amine; no change was observed when the tubes were heated to 100° for short periods, or when traces of $SiH_3{\cdot}NMe_2$ or $MeNH_2$ were included. Tubes containing the amine and COS or CS_2 after standing at room temperature for six weeks showed a strong resonance at $\tau = 6{\cdot}78$, assigned to SiH_4,[10] with other peaks at $\tau =$ *ca.* 7·4 (MeN) and *ca.* 5·6 (HSiN), whose areas were in approximate ratio 3 : 2. These can be assigned to the CH and SiH resonances of polymeric $(CH_3{\cdot}N{\cdot}SiH_2)_n$.

TABLE 2

Proton resonance results for adducts between *NN*-dimethylsilylamine and carbon oxides and sulphides

Reactants	Solvent/standard	τ (CH) ±0·03 p.p.m.	$J(^{13}CH)$ ±0·5 c./sec.	$J(^{15}NCH)$ ±0·06 c./sec.	τ(SiH) ±0·03 p.p.m.	$J(^{29}SiH)$ ±0·5 c./sec.
SiH_3NMe_2	TMS/TMS	7·51	134·6	⩽0·2 [a]	5·64	205·7
	CCl_4/TMS	7·61	135·7	n.o.	5·69	205·1
SiH_3NMe_2/CO_2	CO_2/TMS [b]	7·09	138·6	n.m.	5·55	233·6
	CCl_4/TMS [b]	7·07	n.m.	1·07	5·54	232·8
SiH_3NMe_2/CS_2	CS_2/TMS [b]	6·59	140·1	n.m.	5·63	234·3
	CCl_4/TMS [c]	6·52	n.m.	1·41	5·65	n.m.
SiH_3NMe_2/COS	CCl_4/TMS [c]	6·78 [d]	n.m.	1·34	5·39	235·9
		6·66 [d]		1·42		

[a] In (tetramethylsilane), $J(^{15}NSiH)$ is 5·08 ± 0·06 c./sec.; in CCl_4 (lines broad) $J(^{15}NSiH)$ not observed.[8] [b] Measurements over the range −35 to +20° fall within the stated limits. [c] Measured only at room temperature; spectrum qualitatively unchanged in the range −30 to +20°. [d] No collapse on heating to +60°. n.m. = Not measured. n.o. = Not observed.

Reactions of NN-*Dimethylsilylamine*. (i) CO_2 (2·70 mmoles) was kept with $SiH_3{\cdot}NMe_2$ (1·07 mmoles) at room temperature (15 hr.). A viscous liquid formed, which slowly became a white solid. Non-condensable gas (0·3 mmole) was formed; the other volatile products recovered were SiH_4 (0·74 mmole) (Found: *M*, 33·1. Calc. for SiH_4: *M*, 32·1), identification confirmed spectroscopically, and CO_2 (1·68 mmoles) (Found: *M*, 43·2. Calc. for CO_2: *M*, 44·0), identification confirmed spectroscopically. The combining ratio (amine to CO_2) is 1·05 : 1. In another experiment, CO_2 (0·98 mmole) and SiH_3NMe_2 (3·03 mmoles) were allowed to react as above. No non-condensable gas was detected; the volatile products consisted of SiH_4 (0·35 mmole; identified spectroscopically) and SiH_3NMe_2 (1·96 mmoles) (Found: *M*, 73·8. Calc. for C_2H_9NSi: *M*, 75·1). The involatile liquid residue slowly liberated more SiH_4 on standing (total SiH_4 = 0·76 mmole); the combining ratio is 1·09 : 1. When equimolar quantities of the reactants were taken initially, only SiH_4 (67% of the original silicon) was recovered; in a reaction between SiD_3NMe_2 and CO_2, only SiD_4 was evolved, and no SiD_3H could be detected spectroscopically. The n.m.r. spectra of mixtures of CO_2 and SiH_3NMe_2 in CCl_4 or in excess of CO_2 did not show peaks corresponding to the resonances of the amine itself, even immediately after first melting at −30 to −40°. In addition to the resonances set out in Table 2, a peak at $\tau = 6{\cdot}78$, not present in the spectra of freshly-melted samples, grew in intensity with time and was assigned to SiH_4.

(ii) CS_2 (2·86 mmoles) and SiH_3NMe_2 (0·97 mmole) were allowed to react as above; a yellow liquid formed, and on removing the volatile material, identified as CS_2 (1·95 mmoles) spectroscopically, a white *solid* remained (Found: SiH, 1·97. $C_3H_9NS_2Si$ requires SiH, 1·99%). The combining ratio is 1·03 : 1. In a similar experiment, CS_2 (0·94 mmole) and SiH_3NMe_2 (2·94 mmoles) gave SiH_4 (0·41 mmole; identified spectroscopically) and SiH_3NMe_2 (2·01 mmoles) (Found: *M*, 77·3. Calc. for C_2H_9NSi: *M*, 75·1) as volatile products (combining ratio 0·99 : 1). The n.m.r. spectra of solutions of SiH_3NMe_2 in excess of CS_2 gave only peaks at the positions indicated in Table 2, even at −40°, but the spectra of mixtures of CS_2 and $SiH_3{\cdot}NMe_2$ in CCl_4 at −20° corresponded initially with that of the starting amine; after standing at room temperature (2 days), the tube gave the spectrum of the products.

(iii) COS (2·11 mmoles) and $SiH_3{\cdot}NMe_2$ (0·95 mmole) were allowed to react as described above; a white solid formed. The volatile products consisted of SiH_4 (0·41 mmole; identified spectroscopically) and COS (1·15 mmoles) (Found: *M*, 58·7. Calc. for COS: *M*, 60·1); the combining ratio was 0·99 : 1. In a similar experiment, COS (0·93 mmole) and $SiH_3{\cdot}NMe_2$ (2·03 mmoles) gave SiH_4 (0·49 mmole; identified spectroscopically) and SiH_3NMe_2 (0·95 mmole) (Found: *M*, 74·5). The combining ratio is 1·16 : 1. Satisfactory n.m.r. spectra of mixtures of SiH_3NMe_2 and COS in excess of COS could not be obtained, because of the irreversible formation of solid even at low temperatures; when mixtures of the two reactants in CCl_4 were first melted, a broadened spectrum roughly corresponding to that of the starting amine was obtained at −30°, but after standing at room temperature (3 hr.) the tube gave the spectrum of the products.

Infrared Spectra.—Roughly 10% solutions of the three adducts were made up by distilling the reactants in appropriate quantities into CCl_4; the solutions were transferred to standard liquid cells inside a dry-bag filled with N_2. The following bands were observed:

(i) For $Me_2N{\cdot}C(O)OSiH_3$: 3200(mw), 3050(m,sh), 2970(s), 2900(ms,sh), 2810(m), 2215(vs), 1710(vs), 1650(s,sh), 1500(vs), 1460(s), 1405(vs), 1280(s), 1210(vs), 1070(m,sh), 1048(s), 953(vs), 910(s), 865(s), 710(s).

(ii) For $Me_2N{\cdot}C(O)OSiD_3$: 2930(s), 1720(vs), 1610(s), 1500(vs), 1450(s), 1400(vs), 1280(s), 1200(vs), 1045(s), 890(s), 870(s), 856(s), 698(s).

(iii) for $Me_2N{\cdot}C(S)SSiH_3$: 2950(s), 2220(s), 2160(s), 1500(s), 1410(ms,sh), 1390(s), 1255(s), 1155(s), 1057(ms), 1010(s), 995(s,sh), 945(s), 915(s), 895(s), 880(s,sh), 705(m).

(iv) For $Me_2N{\cdot}C(S)SSiD_3$: 2950(s), 1630(s), 1600(s), 1510(s), 1415(s), 1385(s), 1260(s), 1155(s), 1060(ms), 1007(s), 980(ms), 915(m), 885(m), 700(m).

(v) For $Me_2N{\cdot}C(S)OSiH_3$: 2960(s), 2900(ms,sh), 2205(vs), 2060(m), 1700(m), 1545(vs), 1470(m), 1405(vs), 1350(m), 1300(vs), 1255(m), 1160(vs), 1060(m), 1030(ms), 975(s,sh), 963(s), 941(vs), 896(s), 835(vs), 728(s), 701(s).

(vi) For $Me_2N{\cdot}C(S)OSiD_3$: 2960(s), 2900(m,sh), 2060(ms), 1700(m), 1630(s,sh), 1610(s), 1585(s), 1550(vs), 1470(m), 1405(vs), 1340(m,sh), 1300(vs), 1255(m), 1215(s), 1160(s), 1060(m), 1020(m), 975(s), 836(s), 698(s).

Ultraviolet Spectra.—Spectra were recorded of solutions in CCl_4, made up as for the infrared spectra; extinction coefficients are not given, as concentrations could not be measured accurately enough.

Compound	Absn. max. ($cm.^{-1}$)
$Me_2N{\cdot}C(O)OSiH_3$	37,800
$Me_2N{\cdot}C(S)SSiH_3$	35,500(sh), 33,700
$Me_2N{\cdot}C(S)OSiH_3$	35,100(sh), 33,600

Preparation of Compounds.—The preparation of the silylamines, and of the ^{15}N-labelled compounds, is described elsewhere;[8] CO_2 and CS_2 were obtained commercially, and COS was made from KNCS and sulphuric acid.

Apparatus.—The n.m.r. spectra were recorded using a Varian Associates V-4300B spectrometer, operating at 40 Mc./sec. with flux stabilisation and sample spinning; measurements were made by means of side-bands generated by a Muirhead–Wigan decade oscillator. Errors quoted are statistical mean errors from at least ten individual measurements in each case. Infrared spectra were obtained by means of Perkin-Elmer infraracord spectrometers in the range 4000—670 $cm.^{-1}$; frequencies are probably accurate to ±5 $cm.^{-1}$ in the middle of the range; polystyrene film was used for calibration. Ultraviolet spectra were recorded on a Perkin-Elmer Uvicord spectrometer.

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