"exhaustive trifluoroethoxylation" of 1:6 stoichiometric and excess $N_4P_4Cl_8$–dibenzylamine reaction mixtures gave essentially the same type of GLC traces (3–4 major peaks having retention times 20–60 min at 220 °C) in addition to broad asymmetric peaks with longer retention times. Definite evidence could not be obtained for the precise number and nature of the components present.

The general experimental procedure has been described previously.[10] The preparation of the bicyclic derivative $N_4P_4[N(CH_2Ph)_2]_6N(CH_2Ph)$ (VIII) is described below and details of other reactions are summarized in Table I. The following pure compounds were isolated. $N_4P_4Cl_7[N(CH_2Ph)_2]$ (II): mp 109–110 °C; R_f [TLC(silica gel; eluant benzene–petroleum ether (1:3))] 0.86; ^1H NMR [δ_{CH_2} with $^3J^*(P-H)$ in parenthesis] 4.20 (14.0 Hz); ^{31}P NMR complex multiplet δ −6.0; IR $\nu(P{=}N)$ 1300 cm^{-1}. Anal. Calcd for $C_{14}H_{14}Cl_7N_5P_4$: C, 26.9; H, 2.3; N, 11.2. Found: C, 27.6; H, 2.7; N, 10.6. $N_4P_4Cl_6[N(CH_2Ph)_2]_2$ (III): mp 156–158 °C; R_f 0.80; ^1H NMR 4.12 (14.8 Hz); ^{31}P NMR symmetrical triplet centered at δ −3.9 (A_2B_2 tending to A_4); IR $\nu(P{=}N)$ 1310 cm^{-1}. Anal. Calcd for $C_{28}H_{28}Cl_6N_6P_4$: C, 42.8; H, 3.6; N, 10.7. Found: C, 42.8; H, 3.7; N, 10.5. $N_4P_4Cl_6[N(CH_2Ph)_2]_2$ (IV): waxy solid; R_f 0.76; ^1H NMR 4.24 (15.5 Hz); ^{31}P NMR, see Figure 2; IR $\nu(P{=}N)$ 1315 cm^{-1}. Anal. Found: C, 42.9; H, 3.9; mass spectrum *m/e* (obsd) 784 $(C_{28}H_{28}{}^{35}Cl_5{}^{37}ClN_6P_4)^+$, 691 $(M - CH_2Ph)^+$, 654 $(M - (CH_2Ph) - Cl)^+$. $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (V): mp 114–115 °C; R_f [eluant benzene–petroleum ether (2:3)] 0.69; ^1H NMR 4.27 (14.0 Hz); ^{31}P NMR 2.22; IR $\nu(P{=}N)$ 1300 cm^{-1}. Anal. Calcd for $C_{56}H_{56}Cl_4N_8P_4$: C, 60.8; H, 5.1; N, 10.1. Found: C, 61.4; H, 5.2; N, 10.2. $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (VI): waxy solid; R_f 0.53; ^1H NMR (220 MHz) 4.15 (14.0 Hz), 4.34 (15.0 Hz), 4.40 (15.0 Hz); ^{31}P NMR δ 1.98. Anal. Found: C, 60.3; H, 6.0; N, 10.6. $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (VII): mp 93–95 °C; R_f 0.53; ^1H NMR 4.29 (13.6 Hz); ^{31}P NMR δ 2.01; IR $\nu(P{=}N)$ 1300 cm^{-1}. Mass spectrum *m/e* (obsd) 1104.2360 [M^+ requires 1104.2332], 1069.2650 $(M - Cl)^+$, 1013.1795 $(M - CH_2Ph)^+$. $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII); mp 252–254 °C; R_f 0.83 [eluant benzene–petroleum ether (1:1)]; ^{31}P NMR symmetrical triplet centered at δ 21.3 (A_2B_2 tending to A_4); IR $\nu(P{=}N)$ 1180 cm^{-1}, $\nu[P(2)-N(9)-P(6)]$ 790 cm^{-1}. (Anal., see below.) $N_4P_4(OMe)_6[N(CH_2Ph)_2]_2$ (IX): liquid; ^1H NMR δ_{CH_2} 4.17 (11.0 Hz), δ_{OCH_3} 3.55 (12.5), 3.50 (12.0) ratio 1:2; ^{31}P NMR $\delta_{P(OMe)_2}$ 1.5, $\delta_{P(OMe)[N(CH_2Ph)_2]}$ −4.0, $^2J(P-P) = 65.0$ Hz. $N_4P_4(OCH_2CF_3)_6[N(CH_2Ph)_2]_2$ (X): liquid; ^1H NMR $\delta_{C_6H_5}$ 7.25, δ_{NCH_2/OCH_2} 4.1; ^{31}P NMR $\delta_{P(OCH_2CF_3)_2}$ 5.9, $\delta_{P(OCH_2CF_3)[N(CH_2Ph)_2]}$ −3.6, $^2J(P-P)$ 67.0 Hz. Compounds IX and X were prepared in 70% yield by heating compound III with sodium alkoxide in boiling tetrahydrofuran (96 h). The compounds were GLC pure and further characterized by ^{31}P NMR (A_2B_2 patterns) and ^1H NMR spectroscopy.

Preparation of the "Bicyclic" Derivative, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII). Dibenzylamine (30.0 g, 150 mmol) was added to a stirred solution of $N_4P_4Cl_8$ (I) (2.32 g, 5 mmol) in methyl cyanide at 80 °C. After 160 h, the solvent and unreacted dibenzylamine were distilled under reduced pressure. The sticky residue was heated under reflux with activated charcoal in benzene–petroleum ether (1:1), and the solution was filtered. TLC [eluant benzene–petroleum ether (2:3)] of the filtrate showed that at least six compounds were present. The mixture (4.50 g) was subjected to column chromatographic separation [silica gel (125 g)], and three main fractions (A–C) were collected. Elution with benzene–petroleum ether (2:3) gave fractions A (0.30 g) and B (0.25 g). Fraction A was identified as 2,4,6,8-tetrachlorotetrakis(dibenzylamino)cyclotetraphosphazene (VI); fraction B was an oil, and TLC, elemental analysis, and ^{31}P NMR (complex spectrum from +7 to −6 ppm) suggested a mixture of two (or possibly three) additional tetrakis derivatives. Elution with benzene–petroleum ether (1:1) gave fraction C (0.25 g), which on evaporation of the solvent yielded a sticky solid. After several recrystallizations from methylene chloride–petroleum ether (1:1), the bicyclic derivative, 2,4,4,6,8,8-hexakis(dibenzylamino)-9-benzyl-2,6-epiminocyclotetraphosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII) (mp 252–254 °C), was obtained. (Anal. Calcd for $C_{91}H_{91}N_{11}P_4$: C, 74.7; H, 6.3; N, 10.3. Found: C, 74.3; H, 6.3; N, 10.3.) Elution with benzene gave several minor fractions, but pure compounds could not be obtained from these oily residues. Analytical data for two of these residues clearly showed that chlorine replacement had not exceeded the tetrakis stage. Anal. Calcd for $C_{56}H_{56}Cl_4N_8P_4$: C, 60.78; H, 5.10; N, 10.10. (i) Found: C, 58.48; H, 5.25; N, 8.45. (ii) Found: C, 57.04; H, 5.28; N, 8.81. The ^1H and ^{31}P NMR spectra of these substances show they are mixtures of (chlorodibenzylamino)cyclotetraphosphazene derivatives.

Acknowledgment. The authors thank the University Grants Commission, New Delhi, and the Overseas Development Administration, U.K., for support and Professors A. R. Vasudeva Murthy and R. A. Shaw for their interest. Our thanks are also due to Dr. K. S. Dhathathreyan for assistance in computer simulation.

Registry No. I, 2950-45-0; II, 79448-98-9; III, 79448-99-0; IV, 79449-00-6; V, 79449-01-7; VI, 79516-85-1; VII, 76816-86-2; VIII, 76312-46-4; IX, 79449-02-8; X, 79449-03-9; $N_4P_4Cl_5[N(CH_2Ph)_2]_3$, 79449-04-0; dibenzylamine, 103-49-1.

Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

The Reaction between Sulfur Dioxide and Hexamethyldisilazane. 2. Oxygen Atom Transfer from Sulfur Dioxide

D. W. BENNETT* and L. D. SPICER*

Received July 16, 1981

The new reaction between sulfur dioxide and hexamethyldisilazane, which forms $((CH_3)_3Si)_2O$, $(CH_3)_3SiNSO$, and $NH_4(CH_3)_3SiOSO_2$, is characterized. In this reaction oxygen is transferred to silicon and sulfur from sulfur dioxide, but Si–N bonding is still partially retained. The solid product, ammonium trimethylsilyl sulfite, sublimes readily at ambient temperature but exhibits ionic properties. The variety of products and the overall reaction stoichiometry impose severe restrictions on possible reaction mechanisms. These constraints are discussed, and a consistent reaction scheme is proposed for this facile but unusual reaction.

Introduction

Many amines react with sulfur dioxide to yield stable one-to-one products. In such cases an acid–base adduct is generally proposed as the species initially formed, with the adduct either retaining its donor–acceptor structure[1] (e.g., $(CH_3)_3N + SO_2 \rightarrow (CH_3)_3N{\cdot}SO_2$) or rearranging to form a stable compound in which the proton bound to nitrogen migrates to oxygen (eq 1).[2] In a few instances the rearrangement products have been observed to result in cleavage of SO_2 and

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* Addresses for correspondence: D.W.B., Department of Chemistry and Geology, Clemson University, Clemson, SC; L.D.S., University of Utah.

(1) Burg, A. B. *J. Am. Chem. Soc.* **1943**, *65*, 1629.
(2) Michaelis, A.; Storbeck, O. *Liebigs Ann. Chem.* **1893**, *274*, 192.

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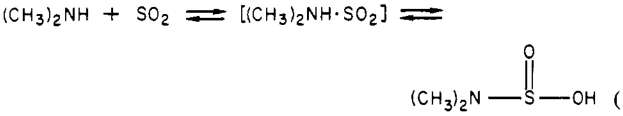

$$(CH_3)_2NH + SO_2 \rightleftharpoons [(CH_3)_2NH \cdot SO_2] \rightleftharpoons (CH_3)_2N{-}\overset{\overset{O}{\|}}{S}{-}OH \quad (1)$$

subsequent oxygen atom transfer to another atom. For example, Hata[3] has concluded that SO_2 reacts with ammonia in the condensed phase to form HNSO and $(NH_4)_2S_2O_5$. Similarly, Nöth and Schweizer[4] have reported the formation of $(R_2B)_2O$ from the reaction of SO_2 with an aminoborane.

In a recent paper[5] we reported the unique reaction between sulfur dioxide and hexamethyldisilazane, $((CH_3)_3Si)_2NH$, in which $(CH_3)_3SiNSO$ was identified as a major reaction product. The formation of this compound clearly requires the removal of oxygen from sulfur and its transfer to another molecule. Thus it appears that oxygen transfer from SO_2 can be facilitated in an appropriate chemical environment. The study of such processes is of general interest and of specific importance in atmospheric chemistry where a variety of sulfur oxides are present. Particularly significant are the problems of acid rain correlated with atmospheric sulfur oxide concentrations and the sizable concentrations of sulfates,[6] particularly ammonium sulfate,[7] found in atmospheric aerosols.

We have now identified the remaining products of this facile reaction between sulfur dioxide and hexamethyldisilazane and have determined its overall stoichiometry. Here we report these results and discuss the complex nature of the stoichiometry and the unique characteristics of the reaction products, which together impose rather stringent constraints on any reasonable mechanism proposed for the reaction.

Experimental Section

General Comments. Reactions were carried out in a 500-mL round-bottom flask fitted with a Teflon stopcock and 9-mm O-ring joint for attachment to the vacuum line. In addition a capped 12-mm O-ring joint was attached to the side of the vessel to facilitate removal of the solid product. Standard vacuum and Schlenk techniques were used in the handling of all reactants and products.[8]

A Gow-Mac Series 550 gas chromatograph equipped with a standard thermal conductivity detector and fitted with a 25 ft × $^1/_4$ in. aluminum column containing 5% SE-30 silicon oil on 45/60 Chromosorb P (acid washed and silanized with Me_3SiCl) was used for separation of liquid products. The column was operated at ca. 60 °C with the injector port at 110 °C and the detector at 130 °C and with a He carrier gas flow rate of 1 mL s^{-1}. Under these conditions retention volumes for $((CH_3)_3Si)_2O$ and $(CH_3)_3SiNSO$ were 282 mL and 408 mL, respectively, relative to the air peak. Pure samples of $((CH_3)_3Si)_2O$ and $(CH_3)_3SiNSO$ were collected by diverting the effluent through a 1-mL glass trap held at liquid nitrogen temperature and fitted with a drying tube containing granular P_2O_5 on the exit to the trap to avoid condensation of water vapor.

Proton NMR spectra were obtained on Varian EM-360 and EM-390 spectrometers. Quantitative studies were performed by dissolving weighed quantities of sample and benzene reference in anhydrous CD_3OD and recording the standard and sample resonances under identical conditions. Peak heights and integrals were normalized to arbitrary units per proton in the standard, allowing for calculation of the relative number of protons in the sample. All chemical shifts were referenced to external $(CH_3)_4Si$.

Infrared spectra were collected on a Beckman IR-20 infrared spectrometer. Spectra of neat liquids were obtained as capillary films between KBr windows. Gases were analyzed in a preevacuated gas cell with a 25-mm diameter and 10-cm path length with KBr windows compression-fitted with O-ring seals. Spectra of solids were obtained from KBr pellets.

Mass spectra were obtained from a Varian 112S mass spectrometer by electron impact ionization of the samples at 60 V. The instrument was calibrated with a perfluorokerosene mass standard.

Data. $((CH_3)_3Si)_2O$ was identified by its characteristic IR spectrum compared with a spectrum from a commercial sample (Aldrich) and its mass spectrum (m/e = 147 (100%), M − 15;[9] m/e = 73 (19.7%), Me_3Si^+). $(CH_3)_3SiNSO$ was likewise identified[5,7] by infrared spectroscopy (2985, 2930, 1415, 1300, 1265, 1140, 1080, 850, 770, 710, 655, 575 cm^{-1}; lit.[10] 2970, 2910, 1420, 1300, 1255, 965, 845, 765, 695, 645, 570 cm^{-1}) and mass spectrometry (m/e = 120 (100%), M − 15; m/e = 73 (5%), Me_3Si^+).

Preliminary characterization of $(CH_3)_3SiNH_4SO_3$ was made on a sample from which all liquid products had been removed under vacuum. The remaining solid was transferred to a Schlenk filter tube, washed with 500 mL of anhydrous ether under dry, oxygen-free nitrogen, and further dried by passing nitrogen through the tube for 2 h. The solid was then transferred to a storage tube, evacuated, and pumped on until approximately one-fourth of the solid had sublimed away, to insure complete removal of volatile residual impurities. Samples of the remaining solid product were transferred to ampules in a glovebox, sealed under nitrogen, and submitted for elemental analysis (Dornis and Kolbe[11]). Anal. Calcd for $C_3H_{13}NO_3SSi$: C, 21.03; H, 7.65; N, 8.17; O, 28.02; S, 18.72; Si, 16.40. Found: C, 20.50; H, 7.25; N, 10.59; O, 27.47; S, 18.30; Si, 15.89. IR (KBr pellet): 3640–2400 (vbr), 1390, 1170, 1080, 1065, 975, 660, 625, 560, 440 cm^{-1}.

Results

Reaction Products. SO_2 reacts readily with $((CH_3)_3Si)_2NH$ to form a solution containing two liquid products, 1,1,1-trimethyl-*N*-sulfinylsilanamine ($(CH_3)_3SiNSO$) and hexamethyldisiloxane ($((CH_3)_3Si)_2O$).[5] In addition a white solid is formed, which has an appreciable solubility in the liquid mixture. Although the structure of the solid was not unequivocally assigned in this work, elemental analysis suggests an empirical formula,[12] $(CH_3)_3SiNH_4SO_3$, which is consistent with a formula weight of 171 or a higher integral multiple. Quantitative proton NMR gives a verifying value of 161 (±10%), on the basis of one trimethylsilyl group per molecule. The solid product exhibits some rather unique physical properties, including a very low bulk density and a vapor pressure of more than 1 torr at 25 °C.[13] This substance sublimes so readily that it is easily moved from trap to trap on the vacuum line, suffering little (if any) decomposition in the process. It is very soluble in water and methanol, slightly soluble in ethanol, very slightly soluble in acetone, and virtually insoluble in dichloromethane, benzene, toluene, cyclohexane, pentane, ether, and acetonitrile. In effect $(CH_3)_3SiNH_4SO_3$ has a vapor pressure indicative of a volatile molecular solid, and yet it displays solubility properties that strongly suggest that it is ionic or highly polar. In addition the equivalent conductance in anhydrous methanol was determined to be 77 $cm^2\ \Omega^{-1}\ equiv^{-1}$ indicative of a 1:1 electrolyte.[13]

Reaction Stoichiometry. The stoichiometry of the reaction was determined via quantitative vacuum-line techniques with gas chromatographic and NMR analysis of products. In a typical experiment 1.30 mol of SO_2 was condensed into a reaction vessel fitted with a Teflon stopcock and containing

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(3) Hata, T. *Tohoku Daigaku Hisuiyoeki Kagaku Kenkyusho Hokoku* **1964**, *14*, 5.

(4) Nöth, H.; Schweizer, P. *Chem. Ber.* **1964**, *97*, 1464.

(5) Davis, J. F.; Spicer, L. D. *Inorg. Chem.* **1980**, *19*, 2191.

(6) Hofmann, D. J.; Rosen, J. M. *Science (Washington, D.C.)* **1980**, *208*, 1368.

(7) Scott, W. D.; Lamb, D.; Duffy, D. *J. Atmos. Sci.* **1969**, *26*, 727.

(8) Shriver, D. F. "The Manipulation of Air-sensitive Compounds"; McGraw-Hill: New York, 1969.

(9) The absence of a parent ion is common for compounds containing the trimethylsilyl group, the M − 15 ion often being the predominant species. See, for example: Pierce, A. E. "Silylation of Organic Compounds"; Pierce Chemical Co.: Rockford, Ill., 1968; pp 34–35.

(10) Schere, O. J.; Schmitt, R. *Chem. Ber.* **1968**, *101*, 3302.

(11) In this analysis oxygen was determined by difference. An earlier analysis by Galbraith Laboratories, Inc., gave the following: C, 20.27; H, 7.87; N, 9.60; O, 27.77; S, 19.01; Si, 15.27.

(12) The solid has been characterized further and positively identified elsewhere.[13]

(13) Bennett, D. W.; Spicer, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 5522.

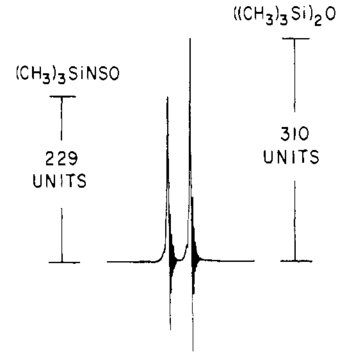


Figure 1. ^{1}H NMR spectrum of the liquid product mixture from the reaction of SO_2 with $((CH_3)_3Si)_2NH$ showing relative peak heights for each component.

0.42 mol of degassed $((CH_3)_3Si)_2NH$ held at −196 °C. The vessel was sealed and allowed to warm to ambient temperature. As soon as the mixture thawed, the formation of a yellow solid began with the yellow color quickly disappearing, leaving a colorless liquid fraction and a white fluffy solid. As reported previously,[5] the reaction occurs rapidly and appears to be essentially complete before the system reaches 0 °C. The unreacted SO_2 was recovered by cooling the vessel to −22 °C and evacuating the flask on the vacuum line through traps held at −60 and −196 °C. The recovered SO_2 was then measured as an ideal gas. In the case cited 0.85 mol of SO_2 was recovered. The results of several such experiments were identical, leading to the conclusion that SO_2 reacts with $((CH_3)_3Si)_2NH$ in a 1:1 molar ratio.

Quantitative, stoichiometric analysis of products was more difficult. The liquid products have a tenacious affinity for the solid, and in addition, both liquid and solid products have similar vapor pressures. Thus separation and quantitative recovery proved to be an unsatisfactory method. Instead the ratio of $(CH_3)_3SiNSO$ to $((CH_3)_3Si)_2O$ in the liquid product mixture was measured via gas chromatography and NMR. The relative thermal conductivities for the pure components were determined by injecting several 10-μL samples into the gas chromatograph and averaging the results. On the basis of the measured density of each liquid ($\rho^{23}_{((CH_3)_3Si)_2O} = 0.763$ g mL^{-1}; $\rho^{23}_{(CH_3)_3SiNSO} = 0.978$ g mL^{-1}) and the detector responses, a thermal conductivity ratio for $(CH_3)_3SiNSO$:$((CH_3)_3Si)_2O$ of 1.29 was measured. Chromatographic analysis of the product mixture corrected for the thermal conductivity differences yielded an average ratio of 1.45 mol of $(CH_3)_3SiNSO$/mol of $((CH_3)_3Si)_2O$.

These results were confirmed with quantitative proton NMR. Figure 1 illustrates the proton NMR spectrum of the liquid product mixture, which exhibits a single sharp resonance for each compound. When normalized to account for differences in the number of protons per molecule, the relative peak heights shown (in arbitrary units) yield a molar ratio for $(CH_3)_3SiNSO$:$((CH_3)_3Si)_2O$ of 1.48:1. The results from these independent studies thus indicate that 3 mol of $(CH_3)_3SiNSO$ are formed for every 2 mol of $((CH_3)_3Si)_2O$.

Although the stoichiometric data suggest that this process may be a typical 1:1 SO_2–amine reaction followed by a simple rearrangment to yield stable products, the ratio of $(CH_3)_3SiNSO$ to $((CH_3)_3Si)_2O$ makes it clear that something more complex is occurring. The composition of the solid product further complicates the picture in that $(CH_3)_3SiNH_4SO_3$ contains four nonmethyl hydrogens. Since $((CH_3)_3Si)_2NH$ is the sole source of such hydrogens, the reaction utilizes at least 4 mol of $((CH_3)_3Si)_2NH$ to form 1 mol of $(CH_3)_3SiNH_4SO_3$. Thus, on the basis of these data, the simplest balanced equation requires 4 mol of SO_2 and 4 mol of $((CH_3)_3Si)_2NH$:

$$4((CH_3)_3Si)_2NH + 4SO_2 \rightarrow 3(CH_3)_3SiNSO + 2((CH_3)_3Si)_2O + (CH_3)_3SiNH_4SO_3 \quad (2)$$

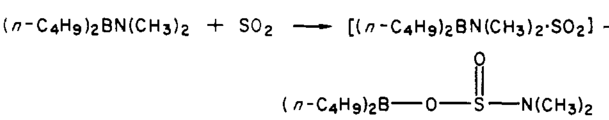
Discussion

Constraints on a Possible Mechanism. The specific mechanistic details of this reaction are undoubtedly complex. Nevertheless, this complexity imposes several useful constraints on proposed mechanisms, which serve to provide insight into the chemistry of sulfur–oxy compounds. They also establish criteria for a postulated reaction scheme, which forms a framework for more detailed mechanistic studies. Such a scheme must be consistent with the relatively complicated stoichiometry including the observation that no additional products are observed. It must explain the oxygen atom transfer phenomenon and at the same time allow for the retention of Si–N bonds, which are generally considered to be much weaker than Si–O bonds. For example, the bond energy of the Si–O bond in $((CH_3)_3Si)_2O$ is approximately 105 kcal/mol, while the energy of the Si–N bond in $((CH_3)_3Si)_2NH$ is only about 75 kcal/mol.[14] The formation of silicon–oxygen bonds in this reaction almost certainly represents a major contribution to the thermodynamic driving force for this process, and yet half of the product molecules contain silicon–nitrogen bonds rather than silicon–oxygen bonds despite the availability of oxygen bonding sites. Finally, the scenario must account for the occurrence of a species that has in some way obtained hydrogen atoms from four *different* hexamethyldisilazane molecules and that, while apparently ionic in the solid state, is capable of subliming readily at ambient temperature.

Formation of $((CH_3)_3Si)_2O$ and $(CH_3)_3SiNSO$. The reaction between SO_2 and (dimethylamino)dibutylborane, $(CH_3)_2NB(n\text{-}C_4H_9)_2$,[4] exhibits some important similarities to the $SO_2/((CH_3)_3Si)_2NH$ reaction. When 2 mol of $(CH_3)_2NB(n\text{-}C_4H_9)_2$ reacts with 1 mol of SO_2, 1 mol of $((n\text{-}C_4H_9)_2B)_2O$ (a boron analogue of $((CH_3)_3Si)_2O$) is formed along with 1 mol of $((CH_3)_2N)_2SO$. The parallel between this reaction

$$2(n\text{-}C_4H_9)_2BN(CH_3)_2 + SO_2 \rightarrow ((n\text{-}C_4H_9)_2B)_2O + ((CH_3)_2N)_2SO \quad (3)$$

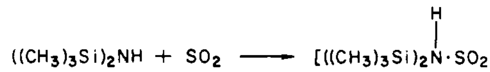
and the reaction under discussion is striking. Nöth and Schweizer[4] have isolated an intermediate, which results from rearrangement of the SO_2–aminoborane adduct in the presence of limited aminoborane:



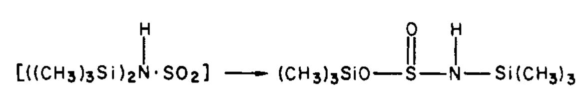
$$(n\text{-}C_4H_9)_2BN(CH_3)_2 + SO_2 \longrightarrow [(n\text{-}C_4H_9)_2BN(CH_3)_2\cdot SO_2] \longrightarrow (n\text{-}C_4H_9)_2B\text{—}O\text{—}\overset{\overset{\displaystyle O}{\|}}{S}\text{—}N(CH_3)_2 \quad (4)$$

The addition of more aminoborane results in cleavage of the S–O bond to form $((n\text{-}C_4H_9)_2B)_2O$.

By analogy with this model, we might expect the initial species in our reaction to be a hexamethyldisilazane–SO_2 adduct, which undergoes a similar rearrangement, probably through a four-center intermediate:



$$((CH_3)_3Si)_2NH + SO_2 \longrightarrow [((CH_3)_3Si)_2\overset{\overset{\displaystyle H}{|}}{N}\cdot SO_2] \quad (5)$$



$$[((CH_3)_3Si)_2\overset{\overset{\displaystyle H}{|}}{N}\cdot SO_2] \longrightarrow (CH_3)_3SiO\text{—}\overset{\overset{\displaystyle O}{\|}}{S}\text{—}\overset{\overset{\displaystyle H}{|}}{N}\text{—}Si(CH_3)_3 \quad (6)$$

The formation of $(CH_3)_3SiNSO$ can then result from an internal rearrangement, perhaps again through a four-center intermediate:

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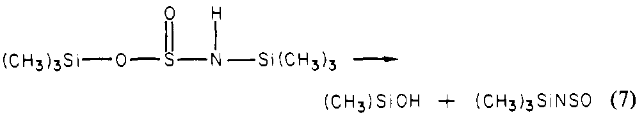
(14) Baldwin, J. C.; Lappert, M. F.; Pedley, J. B.; Treverton, J. A. *J. Chem. Soc. A* **1966**, 1980.



$$(CH_3)_3Si{-}O{-}\overset{\overset{O}{\|}}{S}{-}\overset{\overset{H}{|}}{N}{-}Si(CH_3)_3 \longrightarrow (CH_3)SiOH + (CH_3)_3SiNSO \quad (7)$$

Monofunctional silanols have been shown to condense readily with monofunctional silylamines to form amines and siloxanes:[15]

$$R_3SiOH + R'_3SiNR''_2 \rightarrow R_3SiOSiR'_3 + HNR''_2 \quad (8)$$

Hexamethyldisilazane reacts rapidly and efficiently with compounds containing polar X–H bonds,[16] and since silanol, $(CH_3)_3SiOH$, is even more acidic than methanol[17] it would certainly react immediately with additional $((CH_3)_3Si)_2NH$ present to form hexamethyldisiloxane:

$$((CH_3)_3Si)_2NH + (CH_3)_3SiOH \rightarrow ((CH_3)_3Si)_2O + (CH_3)_3SiNH_2 \quad (9)$$

At this point the mechanism has produced both liquid products observed and an oxygen atom has been transferred from sulfur to silicon. The remainder of the proposed scheme rationalizes the formation of the third reaction product, $(CH_3)_3SiNH_4SO_3$.

Formation of $(CH_3)_3SiNH_4SO_3$. From its empirical formula two molecular structures for the solid product can be written, which are consistent with the ionic characteristics observed in the solid state and the sublimation properties suggestive of a mixture of molecular entities. The first such compound can be considered to be an ammonium bisulfite analogue. Ammonium bisulfite consists of NH_4^+ and HSO_3^- ions in the solid state, and yet has a normal sublimation temperature of 150 °C.[18] It is formed from NH_3, SO_2, and water vapor[19] at ambient temperature, and the solid can be considered to be in equilibrium with these components in the vapor phase. By analogy solid $(CH_3)_3SiNH_4SO_3$ would consist of $(CH_3)_3SiNH_3^+$ and HSO_3^- ions and would be in equilibrium with a vapor phase made up of $(CH_3)_3SiNH_2$, H_2O, and SO_2. It is likely, however, that $(CH_3)_3SiNH_2$ would react rapidly with water to produce $(CH_3)_3SiOH$ and NH_3, and the original material would not be recoverable after repeated sublimations. This is contrary to the experimentally observed results.

A second more plausible possibility is that the solid material is ammonium trimethylsilyl sulfite, $[NH_4][(CH_3)_3SiOSO_2]$. This compound is expected to sublime as $(CH_3)_3SiOH$, NH_3, and SO_2. While silanol reacts with itself to form $((CH_3)_3Si)_2O$ and water, the solid and vapor can exist near equilibrium because the reaction proceeds very slowly even in dilute solutions.[20] Further support[12] that the trimethylsilyl sulfite is the product of choice at this stage derives from consideration of the overall reaction scheme. The formation of $[NH_4][(CH_3)_3SiOSO_2]$ follows logically from the generation of $(CH_3)_3SiNH_2$, the extra intermediate product proposed earlier. $(CH_3)_3SiNH_2$ should react rapidly with the $(CH_3)_3SiOH$ product in (7), giving NH_3 and $((CH_3)_3Si)_2O$:

$$(CH_3)_3SiNH_2 + (CH_3)_3SiOH \rightarrow NH_3 + ((CH_3)_3Si)_2O \quad (10)$$

The NH_3 produced can then form an adduct with sulfur dioxide, which goes on to react with silanol to form the final solid product as in (11):

$$(CH_3)_3SiOH + NH_3 + SO_2 \rightleftarrows [NH_4][(CH_3)_3SiOSO_2] \quad (11)$$

The following "accounting" summary of the proposed reaction scheme reveals that it is consistent with the overall stoichiometry (note that SO_2 is carried through as $\geqslant N{\cdot}SO_2$ for bookkeeping purposes):

$$\begin{array}{l}
4(Me_3Si)_2NH + 4SO_2 \rightarrow 4(Me_3Si)_2NH{\cdot}SO_2 \\
3(Me_3Si)_2NH{\cdot}SO_2 \rightarrow 3Me_3SiNSO + 3Me_3SiOH \\
Me_3SiOH + (Me_3Si)_2NH{\cdot}SO_2 \rightarrow (Me_3Si)_2O + (Me_3SiNH_2{\cdot}SO_2) \\
Me_3SiNH_2{\cdot}SO_2 + Me_3SiOH \rightarrow (Me_3Si)_2O + NH_3{\cdot}SO_2 \\
Me_3SiOH + NH_3{\cdot}SO_2 \rightarrow NH_4Me_3SiOSO_2 \\
\hline
4(Me_3Si)_2NH + 4SO_2 \rightarrow 3Me_3SiNSO + 2(Me_3Si)_2O + \\
\hfill NH_4Me_3SiOSO_2
\end{array}$$

The reaction scheme proposed here is not meant to imply detailed knowledge of kinetic or mechanistic features nor does it exclude the possibility of other schemes, provided that they are consistent with the observed phenomena. It is presented primarily as a framework upon which extensions or modifications may be made. Unequivocal determination of the structure of the solid product is one such study that would be useful in verifying the scheme outlined. Unfortunately the solid is difficult to handle, due in large part to its high volatility, and attempts to grow single crystals for X-ray crystallography have produced solid masses, which appear crystalline but show *no* X-ray diffraction pattern.

The reaction between sulfur dioxide and hexamethyldisilazane provides further evidence that SO_2 can behave as a highly reactive molecule under appropriate conditions. In this single reaction we have observed oxygen atom transfer to both silicon and a second sulfur. The possibility that SO_2 can be induced under mild conditions to form $R{-}SO_3^-$ is significant in that the formation of the trimethylsilyl sulfite ion places sulfur one step closer to sulfate. Sulfites are often used as reducing agents, and it is conceivable that the formation of similar products from oxygen atom transfer reactions might assist in the oxidation of SO_2 to SO_4^{2-}, a phenomenon that could have important environmental implications and should be considered in some detail.

Acknowledgment. We wish to acknowledge experimental assistance from Mr. J. Davis in the early stages of this study. We are also indebted to Dr. Cheves Walling for several helpful suggestions during the course of this work. This work was supported by the U.S. Department of Energy under Grant DE-AC02-76ER02190.

Registry No. SO_2, 7446-09-5; $((CH_3)_3Si)_2NH$, 999-97-3; $((CH_3)_3Si)_2O$, 107-46-0; $(CH_3)_3SiNSO$, 7522-26-1; $NH_4(CH_3)_3SiOSO_2$, 79209-10-2.

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