previously pointed out that such a distortion should have a low-energy barrier for compounds of formulation $Rh_2(\mu\text{-}L)_2L'_4$ based on zero-valent rhodium atoms.[14] The structure of this molecule is essentially the same as what was previously reported for $Rh_2(\mu\text{-}CO)_2[P(C_6H_5)_3]_4$,[15] except for the fact that the latter crystal structure included two CH_2Cl_2 solvent molecules which were within bonding distance of the carbonyl ligands. This solvent interaction resulted in a somewhat elongated carbon-oxygen bonding distance in the phosphine complex compared to the phosphite complex (1.175 (8) Å vs. 1.141 (8) Å, respectively). In the solution state, the solvent molecules were shown to occupy a discrete coordination site, inducing one bridging carbonyl to move to a terminal position. Aside from this solvent interaction, the difference between these two structures can be explained by the larger steric requirement of the $P(C_6H_5)_3$ ligand. For example, the P-Rh-P angle is 103.71 (1)° in the triphenylphosphine complex compared to 98.99 (9)° in the phosphite complex. The rhodium-phosphorus bond distances are significantly shorter in the phosphite compound than in the triphenylphosphine compound (2.253 (2) and 2.256 (2) Å vs. 2.321 (2) and 2.327 (2) Å). This fact is reflective of the more effective bonding of the phosphite ligand to the low-valent metal irrespective of electronic or steric interpretations, a structural feature fully consistent with the chemistries of the phosphite- and phosphine-based rhodium systems. Otherwise, the pertinent features of the structures are the same: Rh-Rh = 2.630 (1) Å, Rh-C = 2.013 (8) Å, and Rh′-C = 2.054 (8) Å for the phosphite complex; Rh-Rh = 2.630 (1) Å, Rh-C = 2.051 (6) Å, and Rh′-C = 1.956 (7) Å for the phosphine complex.

Acknowledgment. This collaborative research was supported by the National Science Foundation (Grant CHE-78-08711). All work at Argonne National Laboratory was performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. The rhodium chloride used in these studies was obtained on a loan grant from Johnson Matthey, Inc. We also thank the Miller Institute for Basic Research in Science for a grant in the form of a Miller Professorship (to E.L.M.).

Supplementary Material Available: A stereoview of $Rh_2(\mu\text{-}CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (Figure 4) and a listing of the observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

---

[14] Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806.

[15] Singh, P.; Dammann, C. B.; Hodgson, D. J. *Inorg. Chem.* **1973**, *12*, 1335.

The Reaction between Sulfur Dioxide and Hexamethyldisilazane. 3. The Characterization of Ammonium (Trimethylsilyl)sulfite

D. W. Bennett[†] **and L. D. Spicer***

Contribution from the Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112.
Received November 26, 1980.
Revised Manuscript Received April 20, 1981

Abstract: The reaction between $((CH_3)_3Si)_2NH$ and SO_2 results in the formation of an ionic solid with empirical formula $NH_4(CH_3)_3SiOSO_2$ which readily "sublimes" at ambient temperature. Although (trimethylsilyl)ammonium bisulfite is a logical choice for a molecular formula, IR, NMR, and XPS data rule out the presence of RNH_3^+ and HSO_3^- ions. These data, along with a consideration of the solution behavior of this unique material, provide strong evidence that the substance is ammonium (trimethylsilyl)sulfite, with the silicon bonded to oxygen rather than sulfur.

In a recent paper[1] we reported the formation of a unique "sublimable" ionic solid from the reaction of sulfur dioxide with hexamethyldisilazane. This deceptively simple reaction occurs rapidly at temperatures below 0 °C to produce $((CH_3)_3Si)_2O$, $(CH_3)_3SiNSO$, and the solid of interest here. The solid formed contains one trimethylsilyl group per mole and has an empirical formala: $C_3H_{13}NO_3SSi$ (**1**). In addition the facile sublimation of this solid makes it an excellent model system in which to study solid-vapor equilibria of inorganic, ionic systems of this type. It should also be noted that this new compound has synthetic utility as a source of silanol, ammonia, and sulfur dioxide, all of which can be generated in situ by gently heating the solid.[1b] While the reaction chemistry of **1** remains to be investigated, the evidence contained herein suggests that the $(CH_3)_3SiOSO_2^-$ is present in alcohol and Me_2SO solutions, probably providing either the (trimethylsilyl)sulfite ion or $(CH_3)_3SiO^-$, an alkoxide analogue, as synthetic intermediates. Because of its interesting physical properties and potential synthetic utility, we have undertaken the task of characterizing this novel substance.

The nature of the $((CH_3)_3Si)_2NH/SO_2$ reaction, coupled with the volatility of the solid, led us to speculate that it was either a (trimethylsilyl)ammonium bisulfite, $(CH_3)_3SiNH_3HSO_3$ or an ammonium (trimethylsilyl)sulfite, $NH_4(CH_3)_3SiOSO_2$. Ammonium (trimethylsilyl)sulfonate, $(CH_3)_3SiSO_3NH_4$, is also a possible structure although the mechanism proposed and thermochemistry suggest the sulfite is preferred.

Of the three possibilities, the sulfite is perhaps the most attractive candidate consistent with a rather complex reaction scheme proposed for the $SO_2/((CH_3)_3Si)_2NH$ reaction.[1] While sublimation properties, reaction stoichiometry, and feasibility of formation appear to make the bisulfite a less likely candidate, definitive evidence to confirm this postulate has not yet been reported due to the unusual physical properties of the solid which make it difficult to handle quantitatively. In addition, as an ammonium salt the solid might be expected to exist as a sulfonate based on organic analogues, but the relative bond energies of silicon-oxygen vs. silicon-sulfur suggest that sulfite formation would be favored. Several attempts to obtain X-ray crystallographic data on **1** have failed, making it necessary to resort to reaction chemistry, conductivity studies, vapor pressure data, and

---

[†] Department of Chemistry and Geology, Clemson University.

[1] (a) Davis, J. F.; Spicer, L. D. *Inorg. Chem.* **1980**, *19*, 2191. Bennett, D. W.; Spicer, L. D. paper 2 in this series, submitted for publication. (b) The vapor-phase chemistry of **1** will be described in a later paper.

0002-7863/81/1503-5522$01.25/0

spectroscopic information in order to determine its structure. Here we give what we believe to be definitive data which identifies and characterizes this interesting new compound.

Experimental Section

The solid product was prepared and purified as previously described.[1] Standard vacuum and Schlenck techniques were used in handling all materials.[2] An independent elemental analysis of the compound was obtained (Dornis and Kolbe Lab., West Germany) which was in agreement with that reported previously.

Equivalent conductance was determined in a Freas-type conductivity cell[3] at 23 °C. Vapor pressures were measured with a McLeod gauge[4] by using an isoteniscope filled with high vacuum oil. The isoteniscope was immersed in a water bath at ca. 60 °C, and pressures were measured as the bath cooled.

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 10-cm path length. The method for obtaining resolved IR spectra of $NH_4(CH_3)_3SiOSO_2$ is described in the text. Spectra of other solids were obtained from KBr pellets.

^1H NMR spectra were collected on a Varian EM-390 spectrometer. ^{13}C and ^{29}Si spectra were obtained on a Varian FT-80 spectrometer. Quantitative measurements were made under identical instrument conditions on the same sample to ensure that the peak integrals were self-consistent. Peak areas were determined directly by measuring the height of the peak and its width at half-maximum. This method was found to be superior to instrument integration with respect to both precision and accuracy. All NMR chemical shifts are referenced to $(CH_3)_4Si$.

X-ray photoelectron spectra of $NH_4(CH_3)_3SiOSO_2$ were measured on a Hewlett-Packard Model 5950B ESCA by using monochromated Al Kα radiation at 800 W. The sample was maintained at −50 °C to avoid sublimation in vacuo. Even under these conditions intensity losses occurred with increased exposure to the X-ray source.

Gas chromatographic data were obtained by using a 25 ft × $^1/_4$ in. aluminum column packed with 5% SE-30 silicone oil on 45/60 Chromosorb P (acid washed and silanized with Me_3SiCl). The column was operated at ca. 60 °C with the injector port at 110 °C, the thermal conductivity detector at 130 °C, and a He-carrier flow rate of 1 mL s^{-1}. Authentic samples of $(CH_3)_3SiOH$ were prepared by mixing $((CH_3)_3Si)_2NH$ with a small quantity of water and immediately injecting a sample taken from the $((CH_3)_3Si)_2NH$ layer. This sample contains both $(CH_3)_3SiOH$ and $((CH_3)_3Si)_2O$ as identified from vapor-phase infrared spectra. Under the conditions described $(CH_3)_3SiOH$ has a retention volume of ca. 120 mL.

X-ray powder patterns were obtained by using a standard 90-mm powder camera. The sample was exposed to filtered (Ni) Cu Kα radiation from an X-ray tube operated at 50 kV and 20 mA for a period of ca. 6 h. $BaSO_3$ (s) was prepared as a reference from BaCl(aq) and Na_2SO_3(aq).

Results

The equivalent conductance of **1** was measured in anhydrous methanol, extrapolated to infinite dilution, and found to be 7.7×10^1 cm^2 Ω^{-1} equiv^{-1}. By comparison, aqueous $[Na][C_3H_7COO]$ has an equivalent conductance of 8.3×10^1 cm^2 Ω^{-1} equiv^{-1},[5] indicating that compound **1** behaves as a 1:1 electrolyte in methanol solution. Unfortunately a direct comparison in water is impossible due to rapid decomposition of the compound.

The vapor pressure of **1** was measured over a 45° temperature range with values varying from 0.5 torr at 4.6 °C to 19.0 torr at 49.0 °C. Figure 1 shows a plot of ln *P* vs. $1/T \times 10^3$ for these data. A linear least-squares fit provides a slope of 7.5 (6)° × 10^3, resulting in a heat of sublimation of approximately 15 kcal mol^{-1}. In comparison, the heat of sublimation of a typical, volatile, molecular solid, naphthalene, is approximately 17 kcal mol^{-1}.[5] Thus, while the multicomponent nature of the sublimation of **1** is a complicating factor, the solid certainly displays vapor-pressure characteristics over this temperature range like those of a molecular solid rather than an ionic solid for which considerably higher vaporization energies are usually found.

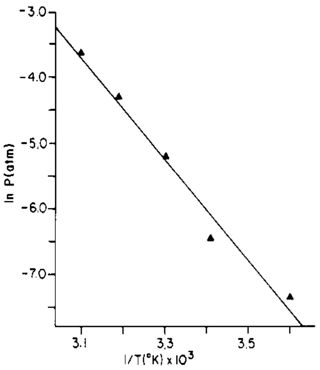


Figure 1. Temperature dependence of the vapor pressure plotted as ln *P* (atm) vs. $1/T$ (K) × 10^3 for the new solid with an empirical formula $C_3H_{13}NO_3SSi$.

Table I. Infrared Spectra of $NH_4(CH_3)_3SiOSO_2$

absorptns, cm^{-1}			
solid film	Nujol mull	KBr pellet	assignmt
3220 sh			$\nu_1 + \nu_5$ (N-H)[a]
3190 vs	3190 s		ν_3(N-H)
3065 vs			ν_1(N-H)
2990 sh	Nujol	~3100	ν_{as}(C-H)
2910 s		vvbr	ν_s(C-H)
2100 vw	2100 vw		$\nu_2 + \nu_6$(N-H)[a]
1840 vw	1840 vw		$\nu_4 + \nu_6$(N-H)[a]
1475 sh			
1450 sh			seen in NH_4Cl[20]
1425 m	Nujol	~1390	ν_4(N-H)
1385 sh		vbr	
1355 w			
1283 sh			
1265 s	1265 m		δ_{as}(C-H)
1160 m	1170 m	1165 m	ν_{as}(S-O)
1075 s	1080 sh	1085 m	ν_s(S-O)
1060 s	1065 s	1065 m	ν(Si-O)
965 m	965 m	975 s	ν(Si-O)
920 sh	890 sh		
865 s	860 s		ρ_{as}(C-H)
820 sh	830 sh		
775 m	775 m		ρ_s(C-H)
	737 w		S-O
708 vw			
672 m	670 s	660 s	ν_{as}(Si-C_3)
630 m	630 s	625 m	S-O
540 m	538 w	560 m	ν_s(Si-C_3)
	510 m		S-O
	440 m		S-O

[a] ν_5 and ν_6 are lattice modes.[20]

Early efforts to obtain resolved IR spectra from KBr pellets were unsuccessful, while those obtained from a Nujol mull resulted in the loss of important absorptions under the Nujol peaks. Excellent spectra were finally obtained by taking advantage of the sublimation properties of the material. A sample of the solid was introduced into a conventional gas IR cell which was then evacuated, leaving pure solid and vapor. The external surface of one of the KBr windows was covered with a plastic sheet to seal it from the atmosphere and avoid condensation of water vapor. This window was then cooled with crushed ice in order to form a film of solid via sublimation. The cell was allowed to warm to ambient temperature, and the spectrum of the solid was easily obtained. All intense absorptions recorded in this manner correspond to those observed from the KBr pellet and Nujol mull. Table I lists the infrared spectrum of the solid along with reasonable spectral assignments. The 1200–900-cm^{-1} region contains peaks strongly suggestive of Si–O and S–O bonding,[6,7] while the

---

[2] Shriver, D. F. "The Manipulation of Air-sensitive Compounds"; McGraw-Hill: New York, 1969.

[3] Daniels, F.; Williams, J. W.; Bender, P.; Alberty, R. A.; Cornwell, C. D.; Harriman, J. E. "Experimental Physical Chemistry"; McGraw-Hill: New York, 1970.

[4] Dodd, R. E.; Robinson, P. L. "Experimental Inorganic Chemistry"; Elsevier: Amsterdam, 1954.

[5] Weast, R. L., Ed. "Handbook of Chemistry and Physics", 53rd ed.; CRC Press: Cleveland, 1972.

[6] Robinson, E. A. *Can. J. Chem.* **1963**, *41*, 3021.

[7] Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1963**, *41*, 2074.

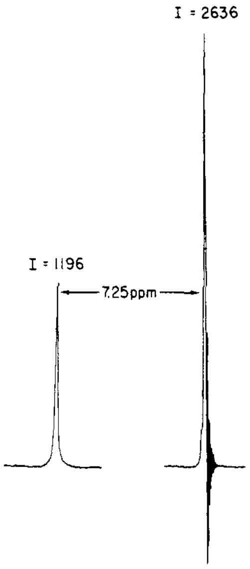


Figure 2. Proton NMR spectrum for the solid of empirical formula $C_3H_{13}NO_3SSi$ in Me_2SO. Calculated integrals (I) are shown above each peak in arbitrary units.

absence of absorptions at or near 2588 and 1123 cm^{-1} (usually strong) expected for S–H stretch and bend, respectively, in HSO_3^- and the absence of a very strong S–O absorption at 1200 cm^{-1}[8] clearly indicate that the bisulfite ion is not present in the solid state. The bands at 3190, 3065, and 1425 cm^{-1} are indicative of $[NH_4]^+$[9] and the absence of an intense absorption at ca. 490 cm^{-1} implies that no Si–S bonding[10] is present.

Raman spectra of the solid were also obtained. The following major bands were observed: 2962 (m), 2906 (s), 1052 (vs), 656 (m), 624 (s), 535 (m), 443 (m), 291 (m), and 247 cm^{-1} (vs).

Proton NMR was obtained from a freshly prepared solution in dimethylsulfoxide, Me_2SO. In addition to water and alcohols reported as solvents earlier,[1] Me_2SO was found to dissolve the solid product providing a solution suitable for measurement even of exchangable protons.[11] Figure 2 illustrates the proton NMR spectrum in Me_2SO with the signals recorded under identical conditions. Both methyl protons and ammonium protons are clearly observed. Protons bound to nitrogen in ions of the form R_3NH^+ have ^1H chemical shifts in the 7.1–7.7-ppm range,[12] indicating that the resonance at δ 7.1 (Me_4Si) is due to a similar species. Calculated integrals are shown above each peak in the spectrum. The $[R_nNH_{4-n}]^+$:$[(CH_3)_3Si]^-$ integral ratio is 0.44, clearly 4:9. Thus $n = 0$, and the resonance is assigned to the ammonium ion.

^{29}Si NMR spectra of **1** in methanol contain a single peak at $\delta(^{29}Si)$ 37.9 (Me_4Si). This result is qualitatively comparable to the ^{29}Si resonance in the similar organosulfite, $(CH_3)_3SiOSO_2CF_3$ of δ 44.6.[13] The ^1H NMR chemical shift of (1) was also recorded in methanol as a single peak at $\delta(^1H)$ −0.10 (Me_4Si); the ^{13}C NMR chemical shift in methanol is also upfield from Me_4Si at $\delta(^{13}C)$ −2.35. The latter result due to the $(CH_3)_3Si$ group along with the facile sublimation properties of this new solid make it an excellent candidate for a solid-state ^{13}C NMR standard.

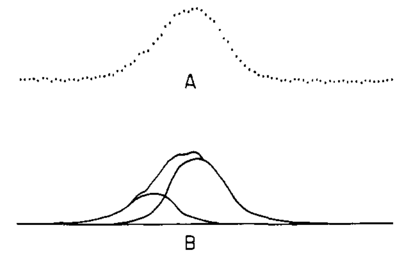


Figure 3. (a) XPS spectrum for the oxygen (ls) electrons in $C_3H_{13}NO_3SSi$. (b) Deconvoluted spectrum for the oxygen (ls) electrons.

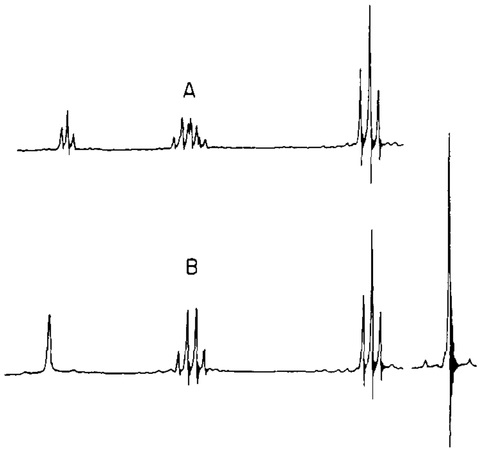


Figure 4. (a) Proton NMR spectrum of anhydrous ethanol. (b) Proton NMR spectrum of $C_3H_{13}NO_3SSi$ in anhydrous ethanol.

Table II. *Infrared Spectrum of $(CH_3)_3SiOH$ and $((CH_3)_3Si)_2O$ from $NH_4(CH_3)_3SiOSO_2$*

absorptn, cm^{-1}	descriptn[20]	absorptn, cm^{-1}	descriptn[20]
3745 ms	ν(O–H), $(CH_3)_3SiOH$	915 sh	ν(Si–O), $(CH_3)_3SiOH$
2985 s	$\nu_{as}(C–H_3)^a$	860 vs	$\rho(C–H_3)^a$
2930 s	$\nu_s(C–H_3)^a$	770 s	ν(Si–O), $(CH_3)_3SiOH$
1350 w	*a*	705 sh	$\nu(Si–C)^a$
1270 vs	$\delta(C–H)^a$	630 w	$\nu(Si–C)^a$
1085 s	ν(Si–O), $((CH_3)_3Si)_2O$		

[a] Seen in spectra of both compounds.

The X-ray photoelectron spectrum of **1** was also obtained and indicates characteristic signals for all elements in the formula. Figure 3A is the XPS spectrum for the oxygen ls electrons in the solid material. Figure 3B shows that this spectrum can be deconvoluted into two peaks with roughly a 2.3:1 integral ratio, indicating two types of oxygens in a 2:1 molar ratio which is consistent with the sulfite structure but not the sulfonate or bisulfite.

The solution behavior of **1** was also studied in order to help characterize the chemistry of this material. When the solid is dissolved in water, in an open container and evaporated to dryness at ca. 100 °C, a colorless nonvolatile residue remains. X-ray powder diffraction data show the product to be $(NH_4)_2SO_4$, indicating that **1** is readily oxidized in oxygenated aqueous solution. Addition of concentrated KOH to an aqueous solution of **1** followed by gentle heating results in the liberation of ammonia or an amine detected as a base by wet litmus.

The addition of a barium chloride solution to aqueous **1** which has been carefully deoxygenated produces a white precipitate characterized as $BaSO_3$ from its X-ray powder pattern which disappears upon addition of concentrated hydrochloric acid. When **1** is added directly to concentrated HCl(aq), SO_2 gas is liberated. The hydrolysis products of **1** were identified from their infrared spectrum following addition of water to a sample of the material under vacuum conditions. All volatile materials generated were pumped through a trap containing KOH(s) to remove water and collected. Table II gives the infrared spectrum of the volatile components from this experiment which identifies $(CH_3)_3SiOH$ and $((CH_3)_3Si)_2O$[14] as the primary components.

The hydrolysis of **1** in water is not paralleled in either ethanol or methanol solvent. Evaporation of a solution of **1** in either

---

(8) Hisatsune, I. C.; Hiecklen, J. *Can. J. Chem.* **1975**, *53*, 2646.

(9) Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *24*, 1253.

(10) Burger, H.; Goetze, U.; Sawondy, W. *Spectrochim. Acta, Part A* **1968**, *24A*, 2003.

(11) Chapman, O. L.; King, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 1256.

(12) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972.

(13) Marsmann, H. C.; Horne, H.-G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27B*, 1448.

(14) Licht, V. K.; Kriegsmann, H. *Z. Anorg. Allg. Chem.* **1964**, *330*, 151.

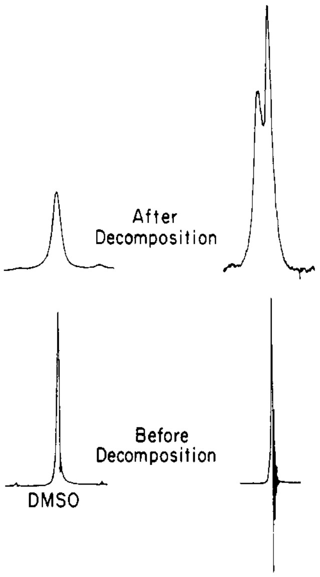


Figure 5. Proton NMR spectra of $C_3H_{13}NO_3SSi$ in Me_2SO before and after decomposition.

alcohol leaves a volatile solid material with a powder pattern identical with that of the original material. Proton NMR spectra of the solid in either alcohol results in a single resonance characteristic of the trimethylsilyl group. Figure 4 illustrates a spectrum of anhydrous ethanol before and after introduction of **1**. Comparison shows that in addition to the absence of the ammonium peak, periods due to the hydroxyl proton on ethanol is lost implying that proton exchange has been initiated with compound **1** in solution. The NMR spectra of alcoholic solutions of **1** remain unchanged over long periods (e.g., months) and no macroscopic physical changes are observed in the solutions.

When **1** is dissolved in $(CH_3)_2SO$, a yellow solution results. There is no visible change in the solution for approximately 1 h, but then a precipitate begins to form slowly. In 24 h precipitation is complete and the solution above the precipitate is once again clear. A proton NMR spectrum of the resulting solution is shown in Figure 5, along with the spectrum from a freshly prepared solution for comparison. The absence of a resonance due to NH_4^+ and a new resonance at $\delta(^1H)$ 0.15 (Me_4Si) are noted in the supernatant liquid. This chemical shift is due to the trimethylsilyl group in either silanol, hexamethyldisiloxane, or both in Me_2SO solution,[15] products with resonances separated by only 0.04 ppm. Gas chromatographic analysis of the supernatant also shows it to contain a mixture of components of $(CH_3)_3SiOH$ and $((CH_3)_3Si)_2O$. An infrared spectrum of the solid residue in this experiment shows it to be $(NH_4)_2SO_3$.[8]

Discussion

The characterization of the new solid material **1** produced in this facile reaction between SO_2 and hexamethyldisilazane has provided considerable insight into the chemistry of sulfur–oxy systems. It is clear that the trimethyl silyl group facilitates reactivity in oxygen atom transfer, sulfur oxidation, and intermolecular rearrangements. It is also evident that this group is responsible in large part for the sublimation properties of this highly volatile solid. On the basis of the combined results reported which often have provided redundant information to verify a conclusion, we are able to identify **1** as ammonium (trimethylsilyl)sulfite, $[NH_4][(CH_3)_3SiOSO_2]$. Below we discuss the results presented in perspective and give the basis for this conclusion.

The physical characteristics of **1** are some of the most intriguing. While it dissolves readily in polar solvents and conducts in methanol, it has sublimation properties similar to those of a volatile covalent solid such as naphthalene. This suggests that the material is largely ionic in solution and in the solid state, but that the solid–vapor equilibrium is characterized by molecular components in the vapor phase. This is similar to the reported sublimation equilibrium for such ionic solids as NH_4Cl and NH_4HSO_3 where the solid vaporizes into two or more different molecular species. We postulate the equilibria given in eq 1–3 by analogy for the three possible molecules consistent with the empirical formula for **1**.

$$[(CH_3)_3SiNH_3][HSO_3] \rightleftarrows (CH_3)_3SiNH_2 + H_2O + SO_2 \quad (1)$$

$$[NH_4][(CH_3)_3SiSO_3] \rightleftarrows (CH_3)_3SiOH + NH_3 + SO_2 \quad (2)$$

$$[NH_4][(CH_3)_3SiOSO_2] \rightleftarrows (CH_3)_3SiOH + NH_3 + SO_2 \quad (3)$$

1 is less favorable at the outset since $(CH_3)_3SiNH_2$ should react rapidly with water in much the same way as $((CH_3)_3Si)_2NH$:[16]

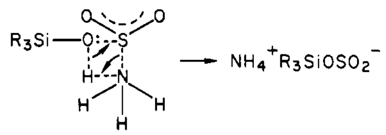
$$(CH_3)_3SiNH_2 + H_2O \rightarrow (CH_3)_3SiOH + NH_3 \quad (4)$$

The Si–O bond is approximately 30 kcal mol^{-1} stronger than the Si–N bond[17] so that (4) should go to completion in the gas phase, thus disrupting the sublimation equilibrium. This deduction, combined with the absence of HSO_3^- in the IR spectrum of the solid and the presence of the ammonium ion as indicated in both IR and NMR spectra, clearly rules out (1) as a possibility. It should also be noted that the trimethylsilyl chemical shift in (1) is actually upfield from $(Me)_4Si$. The methyl protons in $(CH_3)_3SiNH_3^+$ would in all likelihood be *deshielded*, much as in $(CH_3)_4N^+$ compared with $(CH_3)_3N$.[12]

The differentiation between $[(CH_3)_3Si{-}SO_3]^-$ and $[(CH_3)_3SiO{-}SO_2]^-$ is not quite as straightforward. From a thermodynamic viewpoint an Si–O bond is significantly stronger than an Si–S bond[17] making the reversibility of (2) unlikely. The formation of $(CH_3)_3SiOH$ from the sulfonate necessitates the breaking of an Si–S bond and the formation of an Si–O bond. The absence of an intense Si–S band in the infrared spectrum of $[NH_4][(CH_3)_3Si{\cdot}SO_3]$ and the indication from the XPS spectrum that there are two types of oxygen atoms in a 2:1 molar ratio also support the conclusion that solid **1** is the sulfite rather than the sulfonate. $[(CH_3)_3Si{-}SO_3]^-$ would produce a single O(ls) peak since all oxygen atoms are equivalent. Finally the similarity between the ^{29}Si NMR chemical shift of **1** and that of $(CH_3)_3SiOSO_2CF_3$ is consistent with the conclusion that the silicon is bonded to oxygen.

Thus, on the basis of experimental data, we conclude that the compound described herein is ammonium (trimethylsilyl)sulfite. The explicit nature of the sublimation of this compound is currently under investigation. It appears certain that it "sublimes" as three molecular entities, but the nature of the reformation of the sulfite in equilibrium with these molecules is a challenging and as yet unresolved problem. Certainly the process occurs in more than one step. The condensation of silylamines with silanol has been postulated to occur through a four-center mechanism.[18] The formation of $NH_4(CH_3)_3SiOSO_2$ might proceed similarly.

$$NH_3 + SO_2 \rightarrow H_3N{-}SO_2 \quad (5)$$



(6)

In this case we would consider the $R_3SiOSO_2^-$ ion as a weak acid–base adduct of $(CH_3)_3SiO^-$ and SO_2, with the driving force being the formation of an ionic solid.

One further comment regarding the chemistry of the sulfite is appropriate. The solution behavior of $NH_4(CH_3)_3SiOSO_2$ gives interesting information on the relative acidity of $(CH_3)_3SiOH$. In water, reaction 7 occurs as evidenced by $BaSO_3$ precipitation

$$(CH_3)_3SiOSO_2^- + H_2O \rightarrow (CH_3)_3SiOH + HSO_3^- \quad (7)$$

and identification of the volatile products. Thus, as might be expected, water is a stronger acid than silanol. On the other hand,

---

[15] Hampton, J. F.; Lacefiled, C. W.; Hyde, J. F. *Inorg. Chem.* **1965**, *4*, 1659.

[16] Rochow, E. G. "Chemistry of the Silicones"; Wiley: New York, 1951.

[17] Lappert, M. F.; Pedley, J. B.; Treverton, J. A. *J. Chem. Soc. A* **1967**, 1980.

[18] Pike. R. M. *J. Org. Chem.* **1961**, *26*, 232.

$(CH_3)_3SiOSO_2^-$ does not react with ethanol or methanol

$$(CH_3)_3SiOSO_2^- + ROH \nrightarrow (CH_3)_3SiOH + RSO_3^-$$

verifying that silanol is a stronger acid than either ethanol or methanol.

The slow reaction of the sulfite in Me_2SO is also of interest. In Me_2SO solvolysis is unlikely and the observed reaction must occur via another process. One such route is suggested by the aqueous chemistry of ammonia and sulfur dioxide. NH_3 and SO_2 are known to form $(NH_4)_2SO_3$ in the presence of water.[18] If an equilibrium exists in solution between the $NH_4(CH_3)_3SiOSO_2$ and its molecular components NH_3, SO_2, $(CH_3)_3SiOH$, $((CH_3)_2Si)_2O$, and H_2O, the appropriate reactants are available to form the observed precipitate. While silanol ordinarily reacts with itself very slowly to form $((CH_3)_3Si)_2O$ and H_2O, the reaction is extremely condition dependent and is strongly sensitive to surface conditioning of glassware.[19] Under conditions where siloxane is formed from silanol the following reactions are consistent with the observed decomposition products.

$$2(CH_3)_3SiOH \rightarrow ((CH_3)_3Si)_2O + H_2O \tag{8}$$

$$H_2O + 2NH_3 + SO_2 \rightarrow (NH_4)_2SO_3(s) \tag{9}$$

The conclusions drawn here confirm the reaction scheme postulated in our earlier paper on this unique reaction.[1] Furthermore, the identification of the solid product from the reaction now provides us with definitive knowledge of the overall reaction stoichiometry.

$$4((CH_3)_3Si)_2NH(l) + 4SO_2(l) \rightarrow 3(CH_3)_3SiNSO(l) + 2((CH_3)_3Si)_2O(l) + NH_4(CH_3)_3SiOSO_2(s)$$

Acknowledgment. We wish to acknowledge experimental assistance from Mr. S.-Q. Yu, who obtained the Raman spectra, and 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 United States Department of Energy under Grant DE-ACO2-76ER02190.

---

(19) Licht, V. K.; Kriegsmann, H. *Z. Anorg. Allg. Chem.* **1963**, *323*, 252.

(20) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978.

Resonance Raman Studies of Ferric NADH Transients

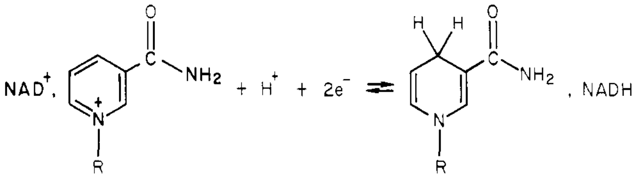
O. Siiman* and R. Callaghan

Contribution from the Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676.

Received February 23, 1981.
Revised Manuscript Received May 11, 1981

Abstract: Resonance Raman spectra of blue and red-violet ferric nicotinamide adenine dinucleotide transients were measured by excitation into absorption bands at 540 and 375 nm. Intense Raman bands observed at 1547 and 1521 cm^{-1} for NADH and its blue ferric transient, respectively, were assigned to nicotinamide ring stretching vibrations. The 26-cm^{-1} lowering of the band position in the transient is related to a decrease in ring bond orders either by complexation to ferric ions or by formation of a half-oxidized free radical intermediate. Resonance enhancement of amide I and nicotinamide ring vibrational modes with excitation into the 375-nm absorption band was linked to differences in the nature of the two excited states.

Nicotinamide adenine dinucleotide (NAD) is a coenzyme that occurs widely in respiratory and photosynthetic systems as a major electron carrier. It is composed of two bases, nicotinamide (3-pyridine carboxamide) and adenine, linked by two sugars and two phosphate groups. The basis of the biological activity of NAD lies in the ability of the pyridine ring to undergo two-electron transfer



At the oxidizing end of the respiratory chain of most organisms, two electrons are transferred from NADH to NADH dehydrogenase,[1] a protein which contains nonheme iron, acid labile sulfur, and flavin mononucleotide (FMN). Since flavins are known to undergo two reversible one-electron reductions, NADH dehydrogenase[2] is believed to be the site at which the electron flow changes from simultaneous two-electron transfer to sequential one-electron transfer. The mechanism by which electrons are transferred from NADH to NADH dehydrogenase is uncertain. The reaction of FMN and NADH in neutral aqueous solution produced absorption spectra[3] characteristic of the flavin free radical, indicating that the flavin functioned as a one-electron acceptor. There was no evidence to show the formation of an NADH free radical species. The addition of sodium nitrosopentacyanoferrate(III) to the FMN-NADH mixture produced a complicated reaction, the net result of which was the oxidation of NADH to NAD$^+$ and reduction of the iron(III) complex. The flavin acted as an intermediary but underwent no overall change.

The direct reaction of NADH with iron(III) has also been investigated.[4,5] When NADH is mixed with ferric perchlorate at pH 3, two short-lived (half-life of several seconds) blue complexes with stoichiometries Fe(NADH) and Fe(NADH)$_2$ were formed. Both have electronic absorption bands at 540 nm (ϵ = 900) and 375 nm (ϵ = 6000). Breakup of the complex produces Fe(II) and NAD$^+$ which do not absorb intensely in the visible spectrum, and no complex is formed by mixing NAD$^+$ with iron(II) or iron(III). Since iron(III) phosphate and iron(III)

---

(1) King, T. E.; Howard, R. L.; Kettman, J., Jr.; Hedgekar, B. M.; Kuboyama, M.; Nickel, K. S.; Possehl, A. E. *BBA Libr.* **1966**, *8*, 441.

(2) Beinert, H.; Palmer, G. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1965**, *27*, 105.

(3) Mayhew, S. G.; Ludwig, M. L. *Enzymes, 3rd Ed.* **1975**, *12B*, 57–118.

(4) Gutman, M.; Margalit, R.; Schejter, A. *Biochemistry* **1968**, *7*, 2778, 2786.

(5) Gutman, M.; Eisenbach, M. *Biochemistry* **1973**, *12*, 2314.

0002-7863/81/1503-5526$01.25/0