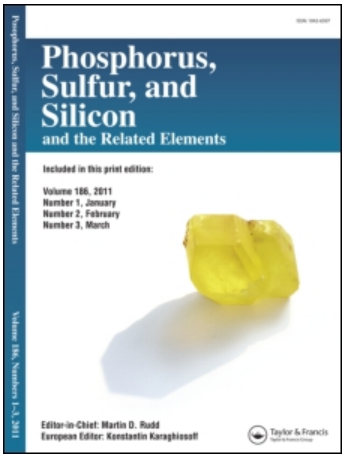

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTIONS OF AMMONIA WITH EXCESS SULFUR DIOXIDE

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To cite this Article Meyer, B. , Mulliken, B. and Weeks, H.(1980) 'THE REACTIONS OF AMMONIA WITH EXCESS SULFUR DIOXIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 8: 3, 291 — 299
To link to this Article: DOI: 10.1080/03086648008078204
URL: http://dx.doi.org/10.1080/03086648008078204

Phosphorus and Sulfur, 1980, Vol. 8, pp. 291–300
0308-664X/80/0803–0291$04.50/0

THE REACTIONS OF AMMONIA WITH EXCESS SULFUR DIOXIDE

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(*Received April 10, 1979; in final form October 26, 1979*)

Ammonia reacts with sulfur dioxide during condensation, even at 10°K, yielding heterogeneous solids containing red $(HNSO)_x$ polymers in which sulfur disproportionates from the oxidation state IV to III and VI, and possibly to other values. Raman spectra indicate that upon warming $(NS)_x$ is formed. The latter is stable at room temperature, but catalyzes the auto-redox decomposition of sulfur dioxide yielding sulfate, sulfamic acid derivatives, dithionate, thiosulfate, polythionate and eventually elemental sulfur. IR spectra show that in rare gas matrices the initial product is HNSO, *cis*-thionylimide, regardless of the molar ratio of reagents. Upon warm-up ammonium disulfide $(NH_4)_2S_2O_5$ is also observed.

INTRODUCTION

The reaction between ammonia and sulfur dioxide yields a variety of products depending on the molar ratio and on other factors. The reaction between excess ammonia and sulfur dioxide yields mainly colorless and white products which are the result of auto-redox reactions of S^{IV} catalyzed by the presence of the nucleophiles. These systems and reactions have been described in a preceding paper.[2] If ammonia reacts with sulfur dioxide in a molar ratio of 1:1, a mixture of white, yellow and red solids form. With excess sulfur dioxide, a deep yellow liquid appears in addition to the colored solids. These reactions have been long recognized, and were first described by Döbereiner in 1826.[3] A comprehensive summary of work before 1958 was given by Becke-Goehring[4] who established the molar ratio of NH_3:SO_2 in many of the solids and identified the hydrolysis products. This paper describes the results of experiments conducted with various ratios of excess sulfur dioxide. Four types of systems were studied: (a) Raman spectra of ammonia and sulfur dioxide vapor co-condensed at 40°K, (b) IR spectra of cold reagent mixtures prepared by the warm-up of rare gas matrices, (c) Raman spectra of the red solids formed from the frozen reagents in sealed ampules, and (d) Raman spectra of the STP products.

EXPERIMENTAL

Low temperature Raman spectra were recorded using samples prepared in a Cryodyne closed-cycle, helium cooled vessel. In the cryogenic experiments, 3 mmole of the undiluted reagent gases were codeposited at a rate of 50 μmole/min on a sapphire window kept at 10°K. IR absorption spectra of matrix samples prepared on a CsBr window in a custom built liquid hydrogen cooled Dewar flask were recorded on a modified Perkin-Elmer 221 grating instrument, as described earlier.[2] Room temperature samples were prepared by condensing the reagents from a vacuum line into 6 mm i.d. × 10 cm long glass tubes which were sealed while the contents were held at 76°K. Raman spectra were recorded on a Ramanor model HG-2 spectrometer, using a Coherent Radiation CR-3 Ar laser. Spectra of the tubes were recorded immediately after preparation and then at increasingly longer intervals over a period of three years to determine slow reactions. All chemicals were analytical grade, and were vacuum distilled. All isotopic species ^{15}N, ^{34}S, D and ^{18}O were at least 95% enriched. Their origin has been given earlier.[2] Several ampules were made for each of the molar ratios SO_2:NH_3 of 30, 15, 7, 3 and 1. Isotopic tubes were prepared with a ratio of 7:1 and 1:1.

RESULTS

1 *Raman Spectra of NH_3 and SO_2 Cocondensed at 10°K*

At a deposition rate of 10 mmole/min, the gases immediately reacted during condensation at 10°K, yielding a light yellow solid which upon warming turned darker red and brownish. The intensity of the sulfur dioxide vibrations depended strongly upon the reagent ratio and was smallest in equimolar solids. During deposition a strong peak grows at 1000 cm^{-1} together with weaker bands at 710, 940, 1215 and 1240 cm^{-1}. All spectra were broad and therefore appeared weak. The relative intensity of peaks changed from sample to sample, and, as a matter of fact, the overall appearance of the spectra changed at different parts of the sample surface, indicating the presence of inhomogeneous mixtures. Upon annealing, all bands broadened. Upon warming up, a large number of partly blended bands appeared with peaks around 116, 320, 440, 530, 653, 697, 1000, 1070, 1130 and 1320 cm^{-1}, Figure 1. However, only one band in the 500–1000 cm^{-1} range was reliably reproducible. This band at 764 cm^{-1} showed a shift of -14 cm^{-1} with $^{15}NH_3$. Upon warming, the sample surface and the appearance of the spectra changed noticeably. However, the substance did not vaporize and remained red-brown at room temperature, indicating an irreversible reaction between the gases. With the addition of a molar ratio of water vapor to the vacuum system, the sample quickly discolored and the bands listed in Table I appeared. We abandoned the bulk cryochemistry technique, because the red solids were not homogeneous and were visibly altered by the laser beam.

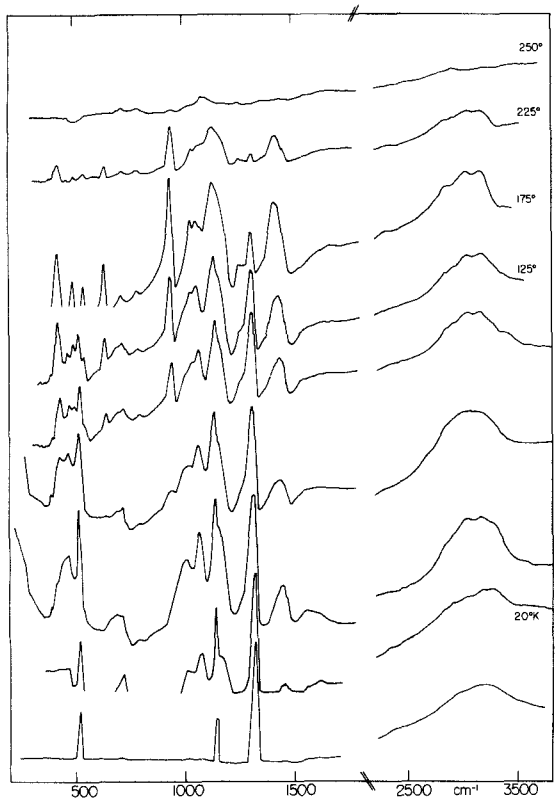


FIGURE 1 Raman spectrum of NH_3 and SO_2 codeposited at 10°K. The sample was annealed at 60°K between deposition, and then brought to room temperature at a rate of about 5°/min.

2 *IR Matrix Isolation Experiments*

If ammonia and sulfur dioxide are diluted with rare gases before condensation at a rate of 30 μmole/

TABLE I

Raman scattering of condensed gases in the 100–1500 cm^{-1} region[a]

Raman peak (cm^{-1}) 10°K	30°K	270°K	Species
		115	S_x (?)
		160	S_x (?)
		220	S_x (?)
		320	$S_2O_3^{2-}$
		440	$S_2O_3^{2-}$
450	450	450	HNSO, SO_4^{2-}
520	(520)	530	SO_2
		550	$NH_3 \cdot SO_3$
		650	$S_2O_3^{2-}$
		698	$NH_3 \cdot SO_3$
700	700	700	$(HNSO)_x$, N_xS_x
		800	$S_2O_6^{2-}$ (?)
911	911	930	HNSO, N_xS_x
		980	SO_4^{2-}
		1000	$S_2O_3^{2-}$
1018	1018	1020	$(HNSO)_x$, $NH_3 \cdot SO_3$
1090	1090	1075	HNSO, $NH_3 \cdot SO_3$
		1130	$S_2O_3^{2-}$
1145	1145	1145	SO_2
		1220	$S_2O_6^{2-}$
	1260	1260	HNSO
1330	(1330)	1320	SO_2

[a] All frequencies are averaged values.

min. at 20°K, the IR spectra shows mainly bands belonging to the unreacted reagents. The low temperature behavior of the samples is very similar to that containing excess ammonia.[2] As soon as the matrix softens or sublimes, i.e. below 40°K, six bands appear at 480, 710, 800, 1040, 1085 and 1260 cm^{-1}. At about 70° to 80°K, depending on the warm-up rate, new bands appear which are different from those observed with excess ammonia.

At high SO_2 ratios, the spectrum is very complex and shows prominent bands at 240, 310, 425, 655, 1022, 1050, 1090 and 1125 cm^{-1}. This spectrum immediately dominates not only because of the number of absorptions, but because of their high intensity.[7] At about 200°K all bands of all species weaken, obviously because at the cryostat pressure of 5×10^{-7} Torr the solid sublimes. At a warm-up rate of 2°/min all spectra disappear before the target reaches room temperature. The samples are cloudy at 20°K, but colorless and remain colorless through the matrix experiments. The spectrum is shown in Figure 1 of the preceding paper. The entire warm-up series was repeated with both dry gases, using ratios of NH_3 to SO_2 of 1:10, 1:7 and 1:1, with an M/R ratio of 300 for Ar and Kr and with the same molar ratios in the presence of 1 molar part water of D_2O. The complex spectrum is due to S_2O_5 and appears both in dry and in wet systems.

3 *Sealed Tubes*

In ampules filled and sealed at 76°K, an exothermic reaction sets in, usually commencing upon warming to −30°C at the interface between the reagents. The reaction products are yellow and red solids which impede the reaction, often dividing the tubes into two separate chambers in which the two reagents can form separate liquid phases, unless the contents of the tubes are forcibly mixed. Originally, we thought that much of the inhomogeneity of the solid phase might be solely due to large concentration gradients at the interface between the reagents. However, even with stirring, we found it difficult to obtain homogeneous products. Instead, the tube contained at least 2 and often 4 solid phases comprising orange, white and often yellow products ranging from dry, dense and amorphous solids to sticky, glossy polymers. Some typical bands of solids are listed in Table II; those of the corresponding liquid, and the isotopic shifts are summarized in Table III.

If excess sulfur dioxide is present, it forms a yellow liquid. The Raman spectrum indicates that all samples are inhomogeneous. Often, spectra of neighboring surface spots differ not only in relative intensity of the bands, but exhibit entirely different spectra, especially in the 500–1000 cm^{-1} range where the N—S band appears. Unlike the ammonia rich tubes, the aging process of sulfur dioxide rich tubes proceeds apparently in two steps which are essentially completed within two weeks. At least, we have not observed any continued changes over a period of 3 years. Table IV lists isotopic shifts of elemental orthorhomic sulfur and sulfur dioxide, and the vibrational modes of some isotropically substituted sulfur dioxide. Figure 3 shows the spectrum of the red solids prepared by combining the reagents at STP in an open glass tube.

DISCUSSION

1 *Matrix Experiments*

The cryoreaction of undiluted reagents at 10°K yields yellow products, all of which have vibrational bands in the 700–1000 cm^{-1} region, which is characteristic for N—S bonds.[8] The sharpest and most reproducible band at 764 cm^{-1} shows a ^{15}N shift of 14 cm^{-1}. This isotope effect corresponds to about 60% nitrogen participation. This band is accompanied by peaks at 453, 900, 1090 and 1250 cm^{-1} and thus belongs to HNSO or a similar species.[5] Due to the excess sulfur dioxide, the solid usually also shows the spectrum of SO_2 with bands at 520, 1145 and 1320 cm^{-1}, as indicated in Table I. Since solids contain heterogeneous mixtures of products, the warm-up will not be further discussed here. At room temperature the spectra show bands which according to their growth rate can be divided into at least 3 groups. Those at 351, 530, 540, 680, 1020 and 1080 cm^{-1} correspond to the spectrum expected for $NH_3 \cdot SO_3$,[6] those at 335, 451, 540, 670, 1002 and 1125 cm^{-1} match the spectrum of $S_2O_3^{2-}$ in frequency as well as intensity.[7] Some solids show bands at 280, 550, 710, 1090 and 1210 cm^{-1} which match the spectrum of dithionate.[7] We studied the hydrolysis products by exposing the red solid in the cryodewar to water vapor, and eventually, by dissolving the solids in excess water. The colored solids all slowly dissolve, forming a yellow solution which eventually discolors. The

TABLE II

Strong Raman spectra in red solids

Peak (cm^{-1})	Fresh[a]	2nd[b]	Old[c]	STP[d]	Species
90			x	x	S_8
130		x	x	x	$(SN)_x$
161			x	x	S_8, $S_x(NH)_{8-x}$
213		x	x	x	$(SN)_x$
225 s			x	x	S_8
261	x	x	x	x	$S_xO_6^{2-}$
280 s	x			x	$S_2O_6^{2-}$
320	x			x	$S_2O_6^{2-}$
339			x	x	$S_2O_3^{2-}$
390				x	$S_x(NH)_{8-x}$
451 s	x	x	x	x	$S_2O_3^{2-}$
460		x	x	x	SO_4^{2-}
480 s			x	x	S_8
500 br	(x)	x	x	x	$S_3O_6^{2-}$
540		x	x	xx	$S_2O_3^{2-}$,(SO_3), $NH_3 \cdot SO_3$
550	x	x	x	xx	$S_2O_6^{2-}$,$(NS)_2$
615		x	xx	xx	$(NS)_x$, (SO_4^{2-})
670	x	xx	xx	xx	$S_xO_6^{2-}$,$S_2O_3^{2-}$
680				x	$NH_3 \cdot SO_3$
705 s, br	x	xx	xx	xxx	$(HNSO)_4$, $(NS)_x$, $S_x(NH)_{8-x}$
710 s	xx	x	x	xx	$S_2O_6^{2-}$
720 br	x	x	x	x	$S_2O_3^{2-}$, $S_xO_6^{2-}$
900				x	$S_x(NH)_{8-x}$
940 s		x	x	x	$(NS)_x$
980	x	x	x	x	SO_4^{2-}, $S(NSO)_2$
1002		x	x	x	$S_2O_3^{2-}$
1020	x	x	x	xx	$NH_3 \cdot SO_3$, HNSO
1040	x	x	x	x	$S_xO_6^{2-}$
1055	x	x	x	x	SO_3^{2-}
1065	x	x	x	x	$S_xO_6^{2-}$
1080	x	x	x	xx	$S_3O_6^{2-}$, $NH_3 \cdot SO_3$
1090	x			x	$S_2O_6^{2-}$
1100			x	x	SO_4^{2-}
1125		x	x	x	$S_2O_3^{2-}$
1210	xx	x		x	$S_2O_6^{2-}$, HNSO
1250				xx	$NH_3 \cdot SO_3$, $S_xO_6^{2-}$
1260	x	x	x	x	$S_xO_6^{2-}$, $S_x(NH)_{8-x}$
1450				x	$NH_3 \cdot SO_3$

[a] 1st day.
[b] 2nd week.
[c] 6 mo and 1 yr.
[d] 1st day prepared at STP. xx and xxx indicate that more than one species is observed.

peaks correspond to thiosulfate, sulfate, and the polythionates, all species identified by Becke–Goehring[4] by wet-analysis in solids formed at room temperature.

2 *Matrix Isolation Study*

The matrix isolation study was conducted, as in the preceding paper, to bring the reagents separately and unreacted to cryogenic temperature.[2] The initial reaction and species are the same as observed in experiments with excess ammonia. However, the end product is different: After depositing, the matrix spectrum is first dominated by the sulfur dioxide yielding bands at 1150, 1330 and 520 cm^{-1}. Upon warming to about 40°K, the matrix vaporizes slowly. The four bands at 430, 900, 1090 and 1250 cm^{-1} and broad bands at 760 and 3300 cm^{-1} appear upon annealing of the matrix and match the 6 bands in the spectrum of an HNSO in an argon matrix,[5] prepared by condensation of HNSO gas made by the reaction of ammonia with sulfurylchloride.[14] This species is stable as a room temperature gas.[5] In the

TABLE III

Strong, persistent Raman peaks in yellow liquid SO_2

Peak cm^{-1}	Intensity	Isotope shift ($-\Delta$) in cm^{-1} ^{34}S	^{18}O	D	^{15}N	mode	NHSO[a]	$(NHSO)_4$[b]
228	2 → 6	6.5	1.8	0	1	S-O		
522	s	4.5	22	0	0	SO_2, ν_3		
700	2 → 6	7.5	4	0	16	S-N		705
784 br	6 → 0		?	?	?	N-S	755	
1040	10	6.5	15	2	26	N-S-O		1020
1088	3	6	20	28	14	H-N-S-O	1086	
1122	1	12	3	0	1.5	N-S-O		
1143	v.s.	8	50	0	0	SO_2, ν_1		
1210	3	24	33	2	2	S-O	1250	1215
1332	s.	14.5	40	0	0	SO_2, ν_2		1340
1665	2	13	73	284	1	N-H		
1726	10	0	8	250	26	N-H		
~3300	10	2	3	~400	8	N-H	3308	

br = broad.
[a] IR peak (cm^{-1}), Ref. 5.
[b] IR peak (cm^{-1}), Ref. 14

cold solid, it is not suppressed by equimolar quantities of water added separately. The complex set of strong bands with peaks at 280, 460, 650, 950, 1040, 1080, 1250 and 2650 cm^{-1} appears above 70°K. It clearly belongs to the bisulfite ion, HSO_3^-, and disulfite, $S_2O_5^{2-}$. These two ions occur jointly and coexist in a complex equilibrium.[8,9] The disulfite ion is one of the strongest Raman scatterers of all oxysulfur anions,[7] and accordingly obscures most other features, especially in the S—O stretch region between 950 and 1300 cm^{-1}. Upon warming to room temperature, the spectrum slowly disappears, as ammonium disulfite apparently reversibly disproportionates into ammonia, sulfur dioxide and water. Disulfite is not only formed when water is present as a reagent, but also by the direct reaction of the reagents:

$$NH_3 + 2SO_2 \longrightarrow HNSO + H_2O \cdot SO_2 \qquad (I)$$

$$SO_2 + H_2O \cdot SO_2 + 2NH_3 \longrightarrow (NH_4)_2S_2O_5 \qquad (II)$$

Reaction I occurs at 30–40°K. The intermediates in this reaction are the acid analogues of those formed in the corresponding reaction with excess ammonia. The water-sulfur dioxide adduct is well known. Its IR or Raman spectrum is the same as that of its components. Reaction II depends on the capture of ammonia by the sulfur dioxide hydrate. The second reaction is limited by ammonia diffusion and thus occurs only at about 60°K to 100°K. In the entire reaction sequence no redox processes are observed, and the products all can be vaporized. Thus, in the matrix system, the products of the ammonia reaction with sulfur dioxide are initially independent of the NH_3:SO_2 ratio and proceed by analogous mechanism throughout the entire temperature range.

3 *Sealed Tubes*

In sealed tubes, the reaction proceeds apparently in a different manner. Heterogeneous solids of various yellow and red hues form promptly upon contact between reagents, very much like in the atmospheric pressure reaction between room temperature gases.[3,4] The spectrum of all tubes is dominated by the three strong bands belonging to SO_2. Table II lists the representative frequencies of solids; Table III those of liquids and the corresponding isotopic mixtures. Isotopic frequencies are believed to be accurate to ± 0.5 cm^{-1}. For SO_2 they match the calculated, theoretical values of Wang[10] closely, better than the earlier data by Grigg[11] and by White.[12]

The spectrum of the yellow liquid changes during the first days after preparation, because new products are formed and because the molar ratio of reagents changes. Both effects help the assignment of bands which are partly blended. Figure 2 shows a typical spectrum. The peaks at 1665, 1210, 1121, 1088 and 700 cm^{-1} all show shifts with $^{15}NH_3$, ^{34}S and ^{18}O, and all except the band at 1040 cm^{-1} show significant ND_3 shifts,

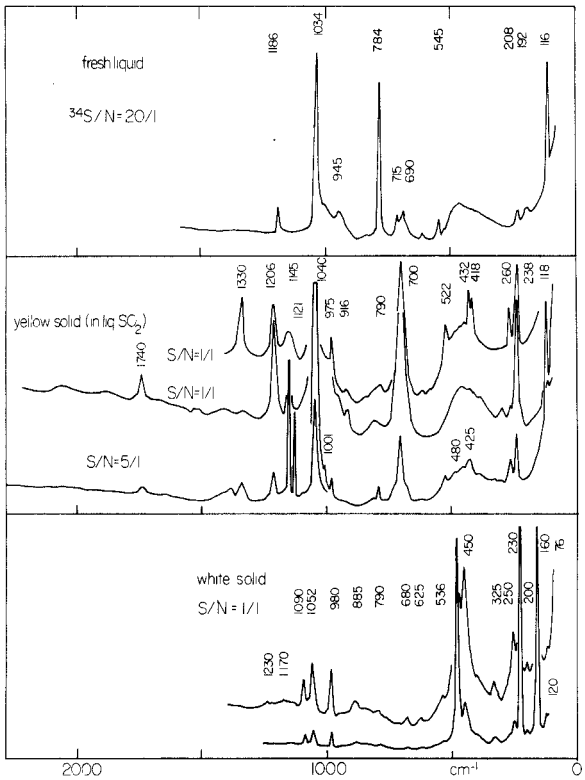
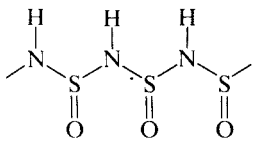


FIGURE 2 Raman spectra of ammonia in excess liquid sulfur dioxide. The sample in Figure 2a is one day old, the one in Figure 2b is one week old, and the white solid in Figure 2c is 6 months old.

Table III. The shifts indicate that the molecular motions are strongly coupled. These bands match the spectrum of HNSO observed before. During the first two days the band at 784 cm^{-1} gives way to a new band at 700 cm^{-1}, while all other peaks remain essentially unchanged. This spectrum is similar to the IR spectrum of $(HNSO)_4$ reported by Fluck[13] and resembles that expected for Schenk's red polymer[14] prepared by reaction of $SOCl_2$ and ammonia with the proposed structure:



(III)

The band at 1088 cm^{-1} exhibits about 54% sulfur participation and 46% oxygen participation. This band corresponds obviously to the symmetric S—O stretch which is strongly coupled to the nitrogen atom. The hydrogen does not participate in this motion, as expected from structure III.

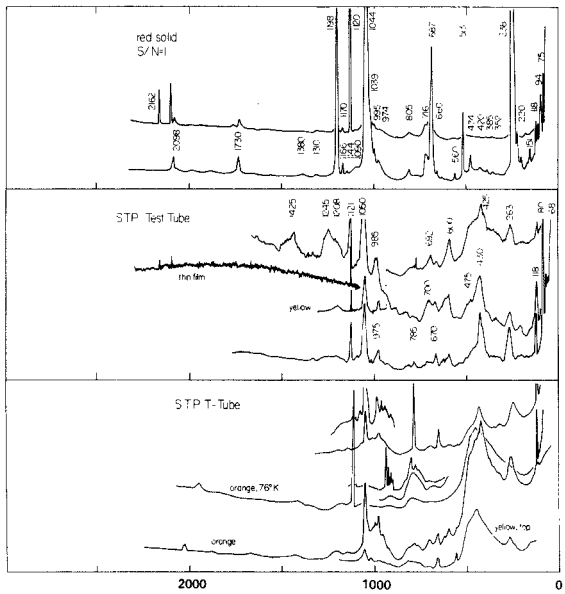


FIGURE 3 Solids prepared at STP. The sample in Figure 3a was stored under dry nitrogen; the one in Figure 3b was quickly quenched to 76°K and later annealed, and the samples in Figure 3c were prepared and stored in open test tubes. The latter spectrum was taken 30 min after preparation.

In the asymmetric stretch at 1332 cm^{-1}, the roles of S and O are reversed as reflected in the isotope shifts. In this motion both nitrogen and hydrogen are passive.

Coupling among neighboring groups occurs frequently in inorganic polyatomics and makes it difficult to identify functional groups, such as the S—S bonds, an entity which could be far more easily identified in organic systems. Likewise, it is not generally possible to correlate observed frequencies with specific force constants, unless the geometry of the molecule is known and a reduced mass can be determined. This prevents unambiguous identification of our species. On the other hand, coupling among neighbors is helpful in our case, because on the basis of the above described isotope shifts of the band at 1088 cm^{-1}, one clearly knows that this molecule contains not only S and O, but also H and N. Thus, the species must be $(HNSO)_n$, $NH_2(SO)_2$, or perhaps $H_2N(SO_2)_2$. Inspection of the ratio of the symmetric to asymmetric stretching S—O suggests that the oxidation state can be either IV or VI, and it is possible that this polymer serves as a redox intermediate. The spectrum contains several other species, the spectra of which change in relation to the above as a function of time and reagent ratio. In the

liquid phase both thiosulfate and dithionate are frequently detected. In the solid the same species appear in mixture with polymeric sulfur nitrides,[16] amidosulfonic acid, sulfate, sulfur imides,[17] $N(SO_2)_4$,[18] $S(NSO)_2$,[19] and the polythionates. The white solid clearly contains HSO_3^-, $S_2O_5^{2-}$, $NH_3 \cdot SO_3$ and some $S_2O_6^{2-}$, as well as other oxysulfur anions, especially sulfate, and also elemental sulfur recognizable by the strong scattering at 474 cm^{-1} and at 220, 161, 159 and 40 cm^{-1}. The Raman spectrum of $^{34}S_8$ is listed in Table IV, as it has not been published before.

A careful analysis of numerous Raman spectra of the red solids obtained at room temperature and STP shows that they contain the same species as sealed tubes, except that the solids slowly hydrolyze in air forming the colorless or light yellow solution already described by Becke–Goehring.[4] A quantitative Raman spectrometric analysis[7] of the red system for establishing the stoichiometry is difficult, because the solids are heterogeneous, the intensity of most N—S compounds is not yet known, and the solvent effect of liquid SO_2 is not known. Furthermore, the ratio of the elements in the various polythionates and polysulfurpolynitrides can be fractional.

For evaluation of the spectral data the thermodynamically possible species must be considered. According to oxidation potential,[13] the following redox reaction products are possible in acidic systems:

$$S^{IV}: \quad SO_4^{2-}(-0.17); \quad S_xO_6^{2-}(-0.51); \quad S_2O_3^{2-}(-0.40); \quad S_x(-0.45); \text{ and } S^{2-}(-0.35) \qquad \text{(IV)}$$

$$N^{III}: \quad N_2(-0.27); \quad \text{and} \quad N_2O(-0.65) \qquad \text{(V)}$$

The products in Tables I–IV, identified by spectral methods, all fit these lists. We have found no indication of N_2 and N_2O, but we have not analyzed the mass spectra of the vapor phase. The experiments indicate that all reaction products are formed by auto-redox reaction of S^{IV}, as is the case with the excess ammonia. However, in the present acidic system S^{III} is capable of entering stable products with nitrogen, and the preferred product oxidation states are apparently S^{III}, S^{VI}, S^0 and S^V, in order of relative abundance.

The reactions leading to red products can be represented by over-all equations of the type

$$6NH_3 + 5SO_2 \longrightarrow \tfrac{1}{2}(N_4S_4) + (NH_4)_2SO_4 + 2NH_4HSO_3 \qquad \text{(VI)}$$

TABLE IV

Raman peaks of orthorhombic sulfur (cm^{-1} ± 0.2)

$^{34}S_8$	Intensity	S_8	Intensity	Shift (cm^{-1})	Assignment
46.2	(78)	48.3	(78)	4.54	
63.1	(15)	65.0	(13)	3.01	
77.8	(12)	80.2	(10)	3.08	
86.3	(20)	88.7	(18)	2.78	ν_9
90.2	(14)	92.4	(12)	2.44	
149.6	(16)	153.8	(16)	2.81	ν_8
152.4	(36)	157.1	(34)	3.08	ν_8
154.5	(41)	159.0	(39)	2.91	
156.3	(30)	161.6	(28)	3.39	
186.6		192.4		3.11	
212.6	(25)	221.2	(23)	4.04	ν_2
216.9	(90)	225.4	(91)	3.92	
242.6	(5)	252.1	(4)	3.91	ν_{11}
427.5	(4)	444.0	(3)	3.86	ν_{10}
443.0	(1)	462.0	(3)	4.29	
454.2	(7)	470.0	(7)	3.48	
459.5	(28)	474.0	(38)	3.15	ν_7, ν_1
607		623		2.64	
797		821		3.01	
821		848		3.29	
850		876		3.06	
867		895		3.23	
908		933		2.75	

for which one can calculate $\Delta H = -182.8$ kcal/mole.[21] Thus, the reaction can be expected to proceed vigorously, as it does. The mechanism can be written as step-wise process:

$$2NH_3 + 2SO_2 \longrightarrow 2NH_2SO_2H \qquad \text{(VII)}$$

$$NH_2SO_2H \longrightarrow NH_4HSO_3 + HNSO \qquad \text{(VIII)}$$

$$nHNSO \longrightarrow (—NH—SO—)_n \qquad \text{(IX)}$$

$$(NHSO)_n \longrightarrow (SN)_x + (NH_4)_2SO_4 + (NH_4)HSO_3 \qquad \text{(X)}$$

The intermediate amidosulfite, $NH_2SO_2^-$, is apparently not stable in the presence of excess SO_2, and since it was also absent in the presence of excess ammonia,[2] it might be difficult to isolate except in rare gases at high M/R. In N_4S_4 and $(NS)_2$ both sulfur and nitrogen have been shown to behave as if in the oxidation state III. The sulfurnitrides formation yields the oxygen and hydrogen necessary for oxidation of sulfur to sulfate, the main oxidation product besides $NH_3 \cdot SO_3$ and S_2O_6. Sulfate and sulfite can be thought of dehydrating the system and keeping it non-aqueous. This prevents hydrolysis of N_4S_4. Sulfur dioxide is known to be compatible with N_4S_4, as it has been used as a solvent to prepare various Lewis acid

complexes.[22] The other oxysulfur anions are equally stable in the presence of N_xS_x, and the tubes can be expected to remain stable indefinitely unless they are broken and S_4N_4 slowly hydrolyzes with moisture to yield polythionate mixtures similar to those observed in the ammonia rich system.[2]

CONCLUSIONS

The matrix work of this and the preceding paper indicates that ammonia and sulfur dioxide react above 30°K with negligible activation energy, and initially form *cis*-thionylimide, HNSO, as the primary product, regardless of the molar ratio of the reagents. The latter is known to form by reaction of ammonia with thionylchloride, and is fairly stable.[4,14] Depending on conditions, HNSO or its ammonium salt polymerizes, yielding red HNSO polymer, or hydrolyzes reforming the reagents. In the reaction of bulk reagents the red polymers are heterogeneous and contain sulfur in more than one oxidation state. Raman spectra indicate the presence of $(NS)_x$ as well as $(HNSO)_x$ and possibly $(NH—SO_2)_x$ or derivatives of the latter. The polymers catalyze decomposition of excess sulfur dioxide into dithionate, thiosulfate, sulfate, polythionates, and also elemental sulfur. The stoichiometry of the heterogeneous reaction is not yet unravelled, nor is the redox-reaction mechanism. However, it is likely that S^{IV} in the polythionylimide disproportionates to S^{III}, which forms insoluble $(NS)_x$ and S^V or S^{VI}. It is well known that S^{IV} slowly disproportionates in aqueous ammonia, yielding a mixture of sulfate, dithionate, thiosulfate and elemental sulfur. The nature and yield of aqueous products depends on concentration, temperature and impurities. At room temperature, the reaction in saturated solution has a half-life of 1–5 years.[21] We observed[2] that the reaction in anhydrous ammonia can proceed via the formation of HNSO, but the products are virtually the same as in the aqueous system, because ammonia attacks the S—N bond. However, the half-life of the autoredox decomposition is reduced to about 1–3 weeks at room temperature. This paper shows that with excess sulfur dioxide the reaction can proceed also via HNSO, but in the acidic system S—N bonds are stable, and $(SN)_x$ polymers form and siphon sulfur-III from the redox system, yielding bright red solids, until all ammonia is consumed. In these systems, the formation of $(NS)_x$ and similar polymers is apparently a driving force and the half-life of anhydrous sulfur dioxide in the presence of ammonia is reduced to seconds. A better understanding of the ammonia-sulfur dioxide system will depend on the isolation and identification of further intermediates, probably in rare gas matrices. The present work indicates that sulfur dioxide and ammonia would be suitable reagents for the direct synthesis of halogen-free, high purity polysulfurpolynitrides.

ACKNOWLEDGMENT

This work was sponsored by the Department of Energy via Lawrence Berkeley Laboratory, Berkeley. The authors wish to thank L. Brewer and R. E. Connick who made their laboratories and equipment available and supported our work in every way. The Cryodyne refrigerator was loaned by N. Bartlett, and ND_3 and $H_2^{18}O$ was provided by G. C. Pimentel.

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