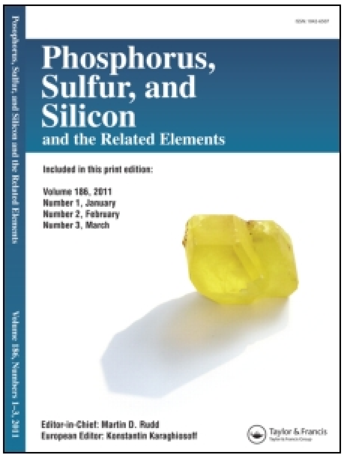

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THE REACTIONS OF SULFUR DIOXIDE WITH EXCESS AMMONIA

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The reaction of sulfur dioxide with excess ammonia was studied during warm-up of rare gas matrices and in sealed pressure tubes containing various isotropic species. In the matrix experiments six IR bands belonging to ammonium thionylimide, NH_4:NSO, were observed in the temperature range between 40°K and 90°K. Above 80°K the spectrum of ammonium sulfite, NH_4SO_3 prevails. In sealed tubes containing liquid ammonia at room temperature several stepwise reactions can be followed. They consist of ammonolysis of SO_2, followed by auto-redox disproportionation of S^{IV} into a range of oxidation states. Raman spectra show the presence of sulfate, dithionate, thiosulfate, and the polythionates. Isotope substitution indicates that ammonia does not participate in redox reactions and acts merely as a nucleophilic catalyst. The composition of the samples changes over a period of at least 2 years. In some tubes with $NH_3:SO_2 < 7$ a spontaneous reaction occurs after 1 1/2 to 2 years and the colorless or pale yellow solution turns a brilliant violet signalling the decomposition of thiosulfate and polythionate into elemental sulfur which reacts with the liquid ammonia yielding negatively charged polysulfide radical ions.

INTRODUCTION

The purpose of this work was to identify the initial step in the reaction of ammonia with sulfur dioxide and to observe intermediates. Sulfur dioxide reacts readily with ammonia forming different products, the composition of which depends on the molar ratio, temperature, and many other factors. The diversity of the potential products was not always recognized, and, thus, the literature contains puzzling and seemingly contradictory observations. For example, for more than 150 years researchers have periodically reported white, yellow and cinnabar colored product mixtures[2–8] which formed even below −60°C and decomposed at room temperature into a mixture of heterogeneous solids. On the other hand, those who measured vapor pressures or observed stoichiometry[8–16] claimed that two simple adducts, $NH_3 \cdot SO_2$ and $(NH_3)_2SO_2$, were produced, both of which could readily and reversibly dissociate into the reagent vapor, with dissociation energies as low as $\Delta H = -9.5$ kcal/mole.

The literature is too extensive to be fully reviewed here. Count Döbereiner[2] reported in 1826 that dry ammonia and sulfur dioxide combined to a brown vapor which condensed as a yellowish solid which in contact with traces of water converted to a colorless salt. Rose carefully repeated his experiment and Forchhammer[3] observed that excess ammonia produced a white solid while excess sulfur dioxide yielded an orange solid. He attempted to determine the stoichiometry and wrote formulas which when translated into current symbols yield the unbalanced equation:

$$4NH_3 + 2SO_2 \longrightarrow (NH_4)_2SO_4 + (NH_2)_2SO \qquad \text{(I)}$$

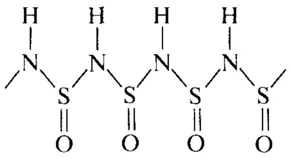
About 50 years later, an extensive treatise on the reaction was published by Schumann[4] simultaneously, but independently, with a study by Divers and Ogawa[5] who found the reaction very complicated. Another 50 years later, Becke-Goehring[6,7] carefully studied the system and identified sulfate, thiosulfate and trithionate among the hydrolysis products, and discovered traces of elemental sulfur, N_4S_4 and N_2S_4 among the thermolysis products. She reviewed results obtained before 1957 in a thorough book[8] and proposed for ammonia-rich mixtures the formation of an adduct followed by formation of ammonium thionylimide. $NH_4(OSN)$, as intermediate:

$$SO_2 + 2NH_3 \longrightarrow SO_2(NH_3)_2 \longrightarrow NH_4(NSO) + H2O \qquad (II)$$

The HNSO molecule was first prepared by Schenk[9] in the gas phase by reaction of thionylchloride with ammonia:

$$SOCl_2 + 3NH_3 \longrightarrow HNSO + 2NH_4Cl \qquad (III)$$

It can be stored in the gas phase for weeks. The IR spectra of isotopically substituted *cis*-thionylimide was studied in rare gas matrices by Spratley[10] who calculated the force field and also studied related photolysis products. Solid HNSO forms a colorless solid which melts at −85°C and polymerizes at −60°C forming a brown substance which is insoluble in most solvents. The formula



(IV)

has been proposed. The monomer can further react with ammonia or sulfur dioxide, with the subsequent formation of imidodisulfinamide or the diammonium salt of the imidodisulfamic acid. With excess sulfur dioxide similar products were obtained, as well as S_4N_4.[8]

The reaction between SO_2 and NH_3 was later studied by Scott and Lamb,[11,12] who found only SO_2 and NH_3 in the vapor above the reaction product, regardless of stoichiometry and color. They deduced the values $\Delta H = 32$ kcal for $NH_3 \cdot SO_2$ and $\Delta H = 62.2$ kcal for $(NH_3)_2SO_2$. Scargill[13] and McLaren[14] also measured vapor pressures to determine thermodynamic values, and Landreth and Hiecklen,[15,16] finally, measured pressures above both dry and wet solids and derived by second law treatment:

$$NH_3 \cdot SO_2(s) \longrightarrow NH_3(g) + SO_2(g) \quad \Delta H = 9.5\,\text{kcal} \qquad (V)$$

Hisatsune and Heicklen[17] then conducted a careful IR study of the reaction between 76°K and room temperature using normal and deuterated ammonia. Among other observations, they found bands which they could assign to an adduct $(NH_3)_2 \cdot SO_2$ which formed above −90°C and decomposed at −50°C to the yellow 1:1 adduct which sublimed at −20°C. In the presence of moisture, the 2:1 adduct converted at −80°C to $(NH_4)_2SO_3$ or to $(NH_4)_2S_2O_5$, both of which were found to sublime at room temperature.

The nature of the initial 1:1 adduct has been repeatedly discussed. In analogy to sulfamic acid, $NH_3 \cdot SO_3$, which is known to be a zwitter-ion,[18] one would expect ammonia and sulfur dioxide to form a charge-transfer complex. Schaefer[19] used the SCF method and experimental data on $(CH_3)_3N \cdot SO_2$ to predict the geometry and the heat of formation of the complex. He found the most likely structure to be the one in which the plane of SO_2 is nearly perpendicular to the ammonia C_3 axis, with an N–S distance of 2.70 A. He calculated the dissociation energy to be either 9.30 or 10.4 kcal/m, values which are astonishingly close to the experimental value of Landreth,[14] listed above.

We wanted to establish whether the divergent physical and chemical observations could be reconciled. As will be shown later, the temperature dependence of the published vapor pressure data shows clearly that ammonia and sulfur dioxide react with each other at room temperature, despite the deceptively low dissociation energy obtained by second law treatment of this data. Accordingly, we found in preliminary matrix experiments of codeposited vapors at 4°K that significant reaction occurs during the condensation of pure vapors, and that a molar ratio of 1:1 yields heterogeneous solids with poorly reproducible spectra and stoichiometry. We further observed that with excess ammonia the reaction products consistently yielded white homogeneous-looking products, while excess sulfur dioxide consistently yielded heterogeneous red solids. This paper describes experiments with excess ammonia. Experiments with excess sulfur dioxide are described in a subsequent paper. The present study consisted of two parts: first, we conducted matrix-isolation experiments in which ammonia and sulfur dioxide were separately diluted with rare gases before condensation. The spectra of warm-up products proved to be too broad for conclusive identification of isotope shifts. We then condensed isotopically substituted ammonia and sulfur dioxide in various molar ratios into Pyrex tubes and followed the spectra of the sealed ampules as a function of time and of the ratio of ammonia to sulfur dioxide at room temperature.

EXPERIMENTAL

Matrix experiments were conducted in a liquid hydrogen cooled Dewar. Spectra were recorded on a modified Perkin–Elmer Infrared Spectrometer 221 grating instrument. Low temperature samples for Raman spectroscopy were prepared with a Cryodyne refrigerator. All Raman spectra were recorded on a Ramanor model HG-2 spectrometer, using either a Coherent Radiation model CR-3 argon laser, or a Spectraphysics Kr laser. Procedures followed standard isolation methods described earlier.[20]

Ammonia, sulfur dioxide and water were codeposited from three jets on a CsBr window at 20°K at a rate of 10 μmole/min. Four concentration ratios were chosen for NH_3:SO_2:H_2O; (a) 10:1:2, (b) 10:1:0, (c) 3:1:0, and (d) 1:1:0. Argon or krypton was used as matrix gas. The rare gas concentration was M/R = 300. Three experiments were performed for each concentration.

Room temperature samples in ampules were prepared by distilling measured amounts of gases, usually between 4 mM and 50 μM, from a vacuum line into 6 mm diameter and 10 cm long Pyrex tubes held at 76°K. Some tubes contained a short section of a glass rod which could later be used to mix the contents by shaking. The methods have been described before.[21] Before assembly the glass was carefully annealed to prevent sharp edges which are known to catalyze decomposition of S_4N_4 and similar metastable materials. The sealed tubes were tempered in a pentane slush or in dry ice-acetone and then slowly allowed to warm up. Several tubes were made for each gas ratio, and the sequence of the gases condensed was changed in different samples.

Sulfur dioxide, Matheson reagent grade, was dried before use. $^{34}SO_2$ and $S^{18}O_2$ were prepared by heating slightly more than the stoichiometric quantity of elemental sulfur with oxygen. The latter was 5N Linde research grade, and 99% enriched $^{18}O_2$ was obtained from BioRad Inc. 5N sulfur was purchased from ASARCO. 98% ^{34}S was obtained from Monsanto Mound Laboratories. Ammonia was triply distilled from Air Products reagent grade tanks. 99% enriched $^{15}NH_3$ and 99% enriched ND_3 were obtained from BioRad.

RESULTS

1 *Matrix IR Spectra*

The spectrum of a matrix prepared at a deposition rate of 30 μmole/min. at 20°K consisted of the broad water absorption at 1600 and 3400 cm^{-1}, the ammonia peaks in the N–H stretch region at 3300 cm^{-1}, and the sulfur dioxide peaks at 520, 1145 and 1330 cm^{-1}, indicating that no reaction had occurred. At higher deposition rates or at a lower M/R ratio, new peaks appeared at frequencies dependent on the ratio of reagents. Upon warming at a rate of about 2°/min to 40°K, the matrix showed new absorption bands. Among these were a fairly sharp absorption at 1085 cm^{-1} with a weaker companion band at 1040 cm^{-1}, a weaker band at 1260 cm^{-1}, a strong and broad band with a double peak at 710 cm^{-1} and 800 cm^{-1}, and a weaker band at 480 cm^{-1}. Upon further warming all these bands became stronger while the matrix gas sublimed. Above 80°K several new bands appear. At high ammonia concentration, the 960, 630 and 490 cm^{-1} bands of sulfite dominate the low frequency range, and between 3000 and 3500 cm^{-1} the NH_3 vibrations appear, usually strongly overlapped. These high temperature bands are complex, and identical with those described by Hisatsune,[17] except that their half-width is substantially smaller. Depending on the condensation conditions and the matrix material, some of the high temperature bands can appear already at 50°K. Above 90°K all bands weaken; above 120°K they all rapidly disappear, because the solids vaporize in the vacuum vessel.

Apparently, addition of water does affect the intermediate species, and the warm-up behavior of dry and wet systems is almost identical, except in the region of the water bands. Thus, the sulfite spectrum appears in both dry and wet systems. This was puzzling, because water is necessary to convert sulfur dioxide to sulfite. A typical matrix experiment is shown in Figure 1. Absorption maxima are listed in Table I for the dry system. The frequencies listed in the Tables are average values for well resolved peaks. They may differ from the peaks observed in mixtures, as indicated in the figures.

2 *Sealed Tubes*

All tubes were prepared at 76°K. During condensation of the second reagent gas, the vapor pressure in the unsealed tube dropped noticeably quicker, regardless of the gas sequence, and a faint crackling sound indicated reaction at the interface between the reagents. However, all samples remained white. After the tubes were sealed they were transferred to a cold bath. Depending on the bath temperature and the warm-up rate, reaction set in at the reagent interface at −100° to −20°C, yielding a fluffy white solid which completely filled the tubes. These samples were difficult to study because the laser beam caused the sample to boil or sublime. However, after a few hours at room temperature, the samples commenced a reproducible, step-wise aging process which facilitated observation. First, the white snow converted to a denser, white solid from which clear, liquid ammonia separated. From this point on, all tubes contained three phases: a white solid, a colorless liquid and a colorless gas. Within two weeks, the

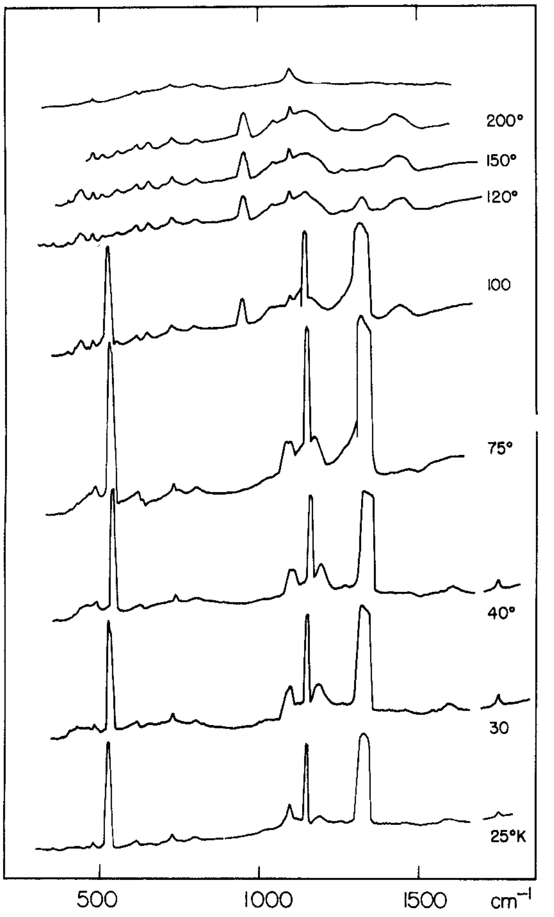


FIGURE 1 IR absorption of the ammonia-sulfur dioxide-argon system during warm-up. The weak peaks at 25°K are due to the M/R = 200 in this experiment. They were absent in experiments with larger M/R.

liquid turned pale yellow. At the same time, cubic crystals, with edges up to 1 mm, formed in the solid phase. At this stage, samples appeared stable for many months, except for one sample tube in which a blue substance formed during the sealing of the Pyrex neck. It will be shown later that other tubes also changed color, but only after one and a half to two years. In some cases the color changed during the recording of Raman spectra. All of these tubes retained a colorless vapor and a colorless, crystalline solid.

Figure 2 shows some spectra representative of the different phases and aging steps of samples containing excess ammonia. The well resolved bands have a half-width of about 20 cm^{-1} and the peaks could be reproduced to within ± 0.5 cm^{-1}. The corresponding Raman shifts and the isotope effects are indicated in Table II.

TABLE I

Strongest IR absorption of the ammonia-sulfur dioxide-argon system during warm-up[a]

Absorption (cm^{-1})			HNSO	Assignment	
20°K[b]	40°K[c]	80°K[c]	(ref. 10)	Species	Mode
	450		448	HNSO	ν_5
		490		SO_3^{2-}	ν_4
520				SO_2	ν_3
		630		SO_3^{2-}	ν_2
	750	754	754	HNSO	ν_6
			(900)	HNSO	ν_4
		960		SO_3^{2-}	ν_1
	1040				
	1085		1083	HNSO	ν_3
1144				SO_2	ν_1
	1255		1248	NHSO	ν_2
1650	1650	1650		NH_3	ν_4
		1685		NH_4^+	ν_3
3210	3210	3210		NH_3	ν_1
3310	3310	3310	3308	HNSO	ν_1
3370	3370	3370		NH_3	ν_3

[a] The frequencies are average values. They may differ from the values listed in figures.

[b] Half width is 5 cm^{-1}.

[c] After the matrix is evaporated the bands are broad.

DISCUSSION

The first question is whether ammonia and sulfur dioxide react at room temperature, or whether they form a reversible adduct. While the reported dissociation energies are divergent and show a confusing spread, the vapor pressure data seems well confirmed.[16] Second law treatment of this data yields a dissociation energy of $\Delta H = 9.5$ kcal/mole, but the temperature dependence of the vapor pressure yields an entropy term $\Delta S°/R$ of only 5.5. This value is unreasonably small compared to a value of about 30, expected from Trouton's rule, or other thermodynamic estimates for the entropy values. Accordingly, third law treatment of the vapor pressure data yields a value of about 24 kcal/mole. This discrepancy clearly shows that the mixture undergoes chemical reaction, as inorganic chemists have claimed all along, since 1828.[1]

1 *Matrix Experiments*

The matrix experiments show that ammonia and sulfur dioxide react as soon as the matrix allows diffusion, even below 40°K. This indicates negligible activation energy. All six bands grow and

TABLE II

Raman spectra of SO_2 in liquid ammonia[a]

	Raman peaks (cm^{-1})				Vibrational
Fresh	1 wk	6 mo	Solid	Species	assignment
	263 s	263	263	$S_xO_6^{2-}$	ν_{6+}
	281 s	281	281	$S_2O_6^{2-}$	ν_3
	320	(320)	—	$S_2O_6^{2-}$	ν_{12}
	330	330	330	$S_xO_6^{2-}$,$S_2O_3^{2-}$	— ν_6
	395 s	—	395	$S_xO_6^{2-}$	—
	430	—	—	SO_3^{2-}	ν_4
	450 s	450 s	450 s	$S_2O_3^{2-}$,(HNSO), SO_4^{2-}	ν_3, ν_2
	540	540	540	$S_2O_3^{2-}$,$S_xO_6^{2-}$	ν_5, ν_4
	625	630	630	SO_4^{2-}	
	674 s	674 s	674 s	$S_2O_3^{2-}$,$S_xO_6^{2-}$,SO_4^{2-}	ν_2, ν_4, ν_3
	710	(710)	710	$(HNSO)_4$, $S_2O_6^{2-}$	ν_2
	900	—	—	HNSO	
	950 br	—	—	SO_3^{2-}	ν_1, ν_3
	981 s	981 s	981 s	SO_4^{2-}	ν_1
	1002	1002	(1002)	$S_2O_3^{2-}$	ν_1
	1021	—	—	HSO_3^-	
1040 vs	1045 s	1045 b	1050	$S_2O_3^{2-}$,$S_xO_6^{2-}$,NH_3	
	1056 s	1050 b	1060	$S_xO_6^{2-}$	ν_2
	1092 s	1092 s	1092	$S_2O_6^{2-}$	ν_1
	1104	1104	1104	SO_4^{2-}	ν_3
	1206	1206	1206	$S_2O_6^{2-}$	ν_{10}
	1240	1240	1240	$S_xO_6^{2-}$	ν_1
	1630	—	—	H-NSO, NH_3	ν_1
	1680	—	1680	NH_4^+	
	3210	—	—	NH_3	
	3294	3294	—	NH_3	
	3376	3376 q	—	NH_3	

[a] The frequencies are average values. They may differ from those observed in complex, blended spectra.

decrease simultaneously, and thus are part of the same system. The intensity and energy indicate that the bands at 1255 and 1085 cm^{-1} belong to the asymmetric and symmetric S—O stretch. The ratio of the two frequencies is 1.16, in accord with the ratio of asymmetric to symmetric S—O vibration observed in other molecules.[22] The bands at 490 cm^{-1} might belong to an S—O bend. While the peak at 1040 cm^{-1} could be caused either by ammonia or S—O, the bands at 700 to 800 cm^{-1} are clearly due to a type of bond not present in the reagents. This spectral region corresponds to N—S single bonds[22] such as found in cyclic or linear sulfamides or sulfamates. A closer inspection of the spectra shows that all six bands fit the IR spectra of matrix isolated HNSO as described by Spratley.[10] It will be shown below that the isotope shifts of the corresponding bands in sealed tubes confirm this assignment, and the 1085 cm^{-1} band shifts with all isotopes of N, S, O and H, confirming the elemental analysis of this species. HNSO, thionylimide, is the imide analogue of SO_2; the S—N bond is 1.512 A, S—O is 1.451 A and the NSO bond angle is 120° according to the microwave spectrum.[23] All isomers of thionylimide, HNSO, N—S—OH and HSNO have been prepared.[10] Of all these species the *cis*-HNSO and its ion is the most stable. The presence of this molecule at low temperature is quite surprising, as its synthesis requires the expulsion of water and requires at least two intermediate intramolecular steps, the formation of an adduct, and the rearrangement to form amidosulfite:

$$NH_3 + SO_2 \longrightarrow NH_3 \cdot SO_2 \longrightarrow NH_2{-}SO_2H \longrightarrow HNSO + H_2O \quad (VI)$$

Since excess ammonia is present, we assume that both HNSO and water immediately convert to the ammonium salt $NH_4 \cdot NSO$. Upon further warming, the IR spectrum of solids containing excess ammonia shows three new bands at 490,

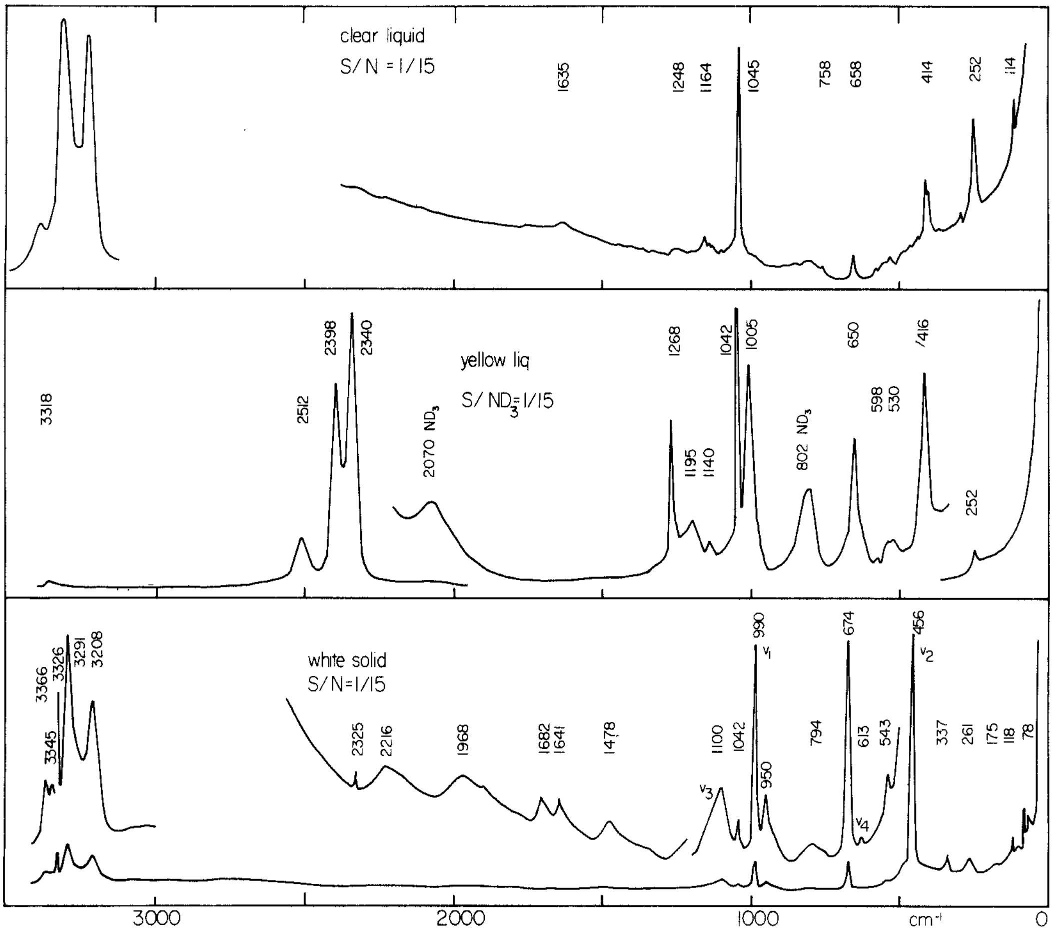


FIGURE 2 (a) Clear liquid on day of preparation; (b) yellowish liquid, 2 weeks old; and (c) white solid after 6 months.

630 and 960 cm^{-1}, as already observed by Heicklen.[17] These bands clearly belong to the sulfite ion. The formation of sulfite from SO_2 and H_2O apparently occurs at about 60°K. The reason for the apparently delayed reaction is probably that the mobility of water is low, and that water is bound in form of adducts with ammonia. Thus, the formation of the sulfite ion is probably preceded by formation of the well established adduct $NH_3 \cdot H_2O$. However, this adduct has the same spectrum as SO_2, and is thus not recognizable by IR or Raman spectroscopy.[24] Since the NH_4^+ vibrations are quite broad we could not conclusively establish at what time this ion first appears. The intermediate bisulfite ion HSO_3^- was not observed. However, the absorption strength of the HSO_3^- vibration is ten fold weaker than that of sulfite.[25]

At first look, it is surprising that the sulfite ion occurs not only in the wet system, but also in carefully dried mixtures of ammonia and sulfur dioxide, and we carefully considered whether the sulfite bands might coincide with those of the as yet unidentified $NH_2 \cdot SO_2NH_4$. We found no bands which could be attributed to this species, but due to the high line width, we could have overlooked this species. Thus, in the absence of positive evidence for other species, the onset of absorption characteristic for HNSO at 40°K suggests the following over-all reaction:

$$4NH_3 + 2SO_2 \longrightarrow NSO \cdot NH_4 + SO_3(NH_4)_2 \qquad \text{(VII)}$$

If one assumes[8] that the first reaction step must be the formation of an adduct $NH_3 \cdot SO_3$, followed by rearrangement to $NH_2 \cdot SO_2H$, the formation of the observed products can be also expressed as the transfer of water between two ammonium amidosulfite molecules:

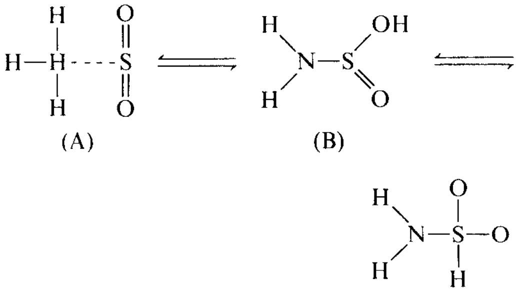
$$2NH_2 \cdot SO_2 \cdot NH_4 \longrightarrow NH_4 \cdot NSO + (NH_4)_2SO_3 \quad (VIII)$$

However, our experiments indicate that the proposed $NH_3 \cdot SO_2$ charge-transfer adduct[9] or the as yet unidentified ammonium amidosulfite is less stable than had been assumed.[8]

Upon warming above −40°C, the sulfite peaks decrease and the products sublime at about −20°C at a cryostat pressure of about 2×10^{-7} torr. Reportedly, HNSO melts at −90°C and polymerizes at −60°C.[8] The fate of this molecule in our systems is not clear, and it is not certain whether under our conditions NH_4NSO sublimes as a monomer or whether it hydrolyses to NH_3 and SO_2 under the influence of water released by sublimation of ammonium sulfite.

2 *Reaction at Room Temperature in the Presence of Liquid Ammonia in Pressure Tubes*

Fresh samples consisting of white, fluffy solids yield poor spectra. These tubes show neither unreacted sulfur dioxide, nor sulfite nor thionylimide. The spectrum is dominated by one strong band at 1040 cm^{-1}, Figure 2. This band shows an ^{18}O shift of 45 cm^{-1} and a ^{34}S shift of 5 cm^{-1}. No deuterium or ^{15}N shifts are measured. The isotope shifts correspond to those expected for the symmetric stretching mode of a free S—O bond and are almost identical with those observed for SO_2 at 1144 cm^{-1}. It is known that the symmetric S—O stretch is one of the most intense of all Raman scatterers.[25] The 1040 cm^{-1} shift is characteristic for three types of functional groups: the SO_3 group of hexavalent single-bonded sulfur such as in polythionates, for SO_2^- as found in charge transfer complexes of organic amines or fluorides,[22, 26–28] or for the thionyls. Since the matching strong polythionate bands at lower frequencies are missing, we believe that the white fluffy solid is due to one of the other species. The simple charge-transfer adduct $NH_3^+ \cdot SO_2^-$ or $(NH_3)_2^+ \cdot SO_2^-$ has been postulated on the basis of the erroneously low second law value of the dissociation energy, $\Delta H = -9.5$ kcal/mole.[15, 16] This value, and the fact that the IR spectrum of the vapor above the solid consists only of the bands of the reagents,[12] is probably responsible for the widely held belief that the adduct should be chemically inert and that its formation could involve only minor structural changes. The following structures can be envisioned for such an adduct:



(IX)

The structure (A) was proposed by Schaefer,[19] whose SCF calculations predict a most likely intermediate distance of 2.7 A with a dipole moment of 4.30 Debye calculated a charge-transfer energy of $\Delta H = 9.5$ kcal/mole, corresponding exactly to the value obtained from vapor pressure measurements.[17] In his structure, the SO_2 plane is perpendicular to the C_3 axis of ammonia. Structure (B) corresponds to amidosulfurous acid of which ammonia-rich systems would form the ammonium salt, and structure (C) corresponds to the same species with the proton attached to sulfur. The latter corresponds to the structure of the bisulfite ion.[24, 29] The structure (A) would be analogous to the sulfamic acid charge transfer complex $NH_3 \cdot SO_3$ in which the entire molecule can assume essentially C_3 symmetry[18] and hydrogen bonding helps the central atoms to establish an N—S distance of 1.764 A. In contrast, all the $NH_2 \cdot SO_2H$ structures are unsymmetrical, and, according to our matrix experiments, apparently unstable as HNSO is formed. Another problem with structure (A) is that one would expect to observe not only the band at 1040 cm^{-1}, but also the other bands of SO_2^- as observed in the organic amines.[26, 30] Furthermore, in view of the ease with which HNSO and SO_3^{2-} form in matrices, it cannot be easily understood why a stable charge-transfer complex (A) $NH_3^+SO_2^-$ could persist at room temperature. However, in our solids, in contact with neighbor molecules, this structure would appear to be an ideal transition state for auto-redox reactions, such as are later on observed. In freshly prepared tubes, neither HNSO nor $(HNSO)_4$ is observed[31] nor $(HNSO)_x$, a deep yellow polymer.[8] The frequency of the 1044 cm^{-1} band is 91% of that of free sulfur dioxide; the reduction factor is identical to that between free SO_3 and $(NH_2)_2SO_2$. This makes it possible that the fluffy white solid is a mixture of ammonium salts of $(NH_2)_2SO_2$, or other similar substances.

Within the first few hours, several other bands appear in all samples. Comparison of tubes with different $NH_3:SO_2$ ratios shows that several reaction products appear almost simultaneously. After about a day, isotopic samples show fine structure in the 1000 cm^{-1} range. Thus, a band at 1001 cm^{-1} appears in ^{15}N marked tubes, and 3 bands at 982, 997 and 1010 cm^{-1} appear in the ^{18}O samples, all in addition to the 1040 cm^{-1} band which is retained. The isotope shifts point towards appearance of an N—S double bond,[22] similar to that of HNSO,[10,31] for which Spratley[10] calculated a force field with 0.4 S$\dot{-}$N participation at its 1080 cm^{-1} band. Some samples show significant amounts of sulfite ion, recognizable by the 620 and 950 cm^{-1} bands. However, the concentration of these species remains low, they quickly stop growing and decrease again in favor of new peaks. Thus, a broad band around 350–450 cm^{-1} appears, and the 990 to 1080 cm^{-1} region shows several overlapping bands. By comparison of concentration and time dependence of the band intensity one can further readily identify bands belonging to thiosulfate and the polythionates. Their presence proves that sulfur (IV) undergoes auto-redox reactions.

Subsequent reaction products are summarized in Table II. Unfortunately, the 1000 cm^{-1} region is crowded with S—O bands belonging to different species. Thus, the strongest bands in many of the expected species are overlapped and obscured, and quantitative analysis[25] of the spectrum is not possible, because sulfate and other oxyanions exceed the solubility limit and crystallize. Furthermore, the solid phase is not homogeneous.

The N—S bands between 600 and 900 cm^{-1} are known to be all broad and thus appear unduly weak. We attempted to correlate and analyze overlapped bands using an electronic curve analyzer and absolute Raman scattering intensities[25] of the various possible components of the product mixtures, but the task is tricky because the different polythionate ions have similar stoichiometries and the spectra overlap in most vibrational modes.[29,32]

The clear, cubic crystals which form in all samples after a few weeks are ammonium sulfate $(NH_4)_2SO_4$. In some samples, both solution and solid phase start showing the strong bands at 710, 1090 and 1210 cm^{-1} characteristic of $S_2O_6^{2-}$. In some tubes, the strong band at 1040 cm^{-1} continues to show for some time a deuterium shift at 798 cm^{-1} and a 4 cm^{-1} shift in ^{15}N, and other features characteristic for $(HNSO)_4$ rings or polymers. However the prominent features, growing in the 200 cm^{-1} and 400 cm^{-1} region, the S—S stretch region, the fine structure and the intermediate bands at 670 cm^{-1}, as well as the S—O stretches at 1120, 1000, 1240–1200 and 1060–1040 cm^{-1} confirm the prevalence of $S_2O_3^{2-}$ and polythionates $3 < n < 6$.

Throughout all stages all samples maintain at least three phases: a colorless vapor phase, a yellowish liquid increasingly saturated with sulfur oxyacids, and the solid phase which is increasingly dominated by SO_4^{2-} but also contains other oxysulfur anions. The liquid contains both reduced sulfur, mainly thiosulfate, and polythionates, as well as SO_4^{2-}. In some tubes dithionate, $S_2O_6^{2-}$ and $NH_3 \cdot SO_3$ were observed. In contrast, we found no evidence for polysulfuropolynitrides. This is not surprising, because $(NS)_4$ and $(NS)_x$ degrade quickly in the presence of aqueous bases and ammonia,[33,34] followed by auto-redox reactions of S^{III}. Likewise, S—N bonds are also readily degraded by sulfite, as are the polythionates. This explains why the polythionates form later than thiosulfate and appear only after sulfite has disappeared. Sulfides were not observed and cannot be present, because they would react with several oxidation states of sulfur, yielding thiosulfate or polythionates or elemental sulfur. The latter and the polysulfides would immediately react with liquid ammonia, yielding the characteristic dark solutions.[35,36]

Inspection of the oxidation potentials[37] shows that in basic medium SO_2 and NH_3 can react with each other yielding that following species:

$$S^{IV}:\quad SO_4^{2-}(0.93);\ S_2O_3^{2-}(0.58);\ S_x(0.66) \text{ and } S^{2-}(5.9) \qquad \text{(X)}$$

$$N^{III}:\quad N_2(0.73) \qquad \text{(XI)}$$

As discussed above, several of these species are mutually exclusive in our systems. Furthermore, nitrogen has never been observed in similar systems, except in electrolysis.[38]

In summary, all of our observed species indicate reactions which can be summarized as auto-redox reactions of sulfur without any reduction or oxidation of ammonia. Ammonia serves merely as a nucleophilic catalyst and as oxygen and proton exchange agent, and participates only in intermediate products:

$$N^{III} + S^{IV} \longrightarrow N^{III} + S^{VI} + S^{V} + S^{I-III} \qquad \text{(XII)}$$

whereby S^{VI} is sulfate or $NH_3 \cdot SO_3$, S^V exists as $S_2O_5^{2-}$, and S^{I-III} is in form of a mixture of thiosulfate and the polythionates $^{-}SO_3{-}S_x{-}SO_3^{-}$. The latter species contain mixed oxidation states. The charge distribution within the chain depends on the chain length.[29] All of these except thiosulfate degrade in the presence of alkaline sulfite, a fact which precludes their formation during the early stage of the $NH_3 + SO_2$ reaction as long as S^{IV} is still present. The same argument explains why the bands at 1040 cm^{-1} in fresh samples cannot be due to polythionates.

The auto-redox reaction of sulfur dioxide to oxyacid consumes water and liberates protons because the products are all reasonably strong acids.[28] Thus, the pH drops. It is well known that the stability of polythionates is strongly pH dependent and that each has a distinct existence range. Thus, during the aging of the samples, the composition of products will change, not only due to redox reactions. As a matter of fact, if the $NH_3 \cdot SO_2$ ratio is small, the pH might drop sufficiently to cause decomposition of thiosulfate and the polythionates to elemental sulfur. This could lead to a sequence of further reactions. Such was indeed observed.

In several tubes with low NH_3:SO_2 ratio the liquid ammonia phase turned slowly yellowish, until after $1\frac{1}{2}$ to 2 years a new reaction set in and the color changed within a day or so to pink, and then, within less than a minute, to red, blue and finally vibrant purple. In some cases, but not in all, the color change occurred during exposure to the laser beam. We had noted that the same brilliant color had appeared in a tube in which some reagent vapor inadvertently came into contact with the hot glass wall shortly after sealing of the sample. This colored solution proved to be stable for at least four years. The bands of the blue solution are listed in Table III together with the bands of a sample produced by dissolving elemental sulfur in a sealed tube containing ammonia. In the latter yellow solid, orthorhombic elemental sulfur dissolves within one or two minutes yielding the same sequence of red, blue and magenta observed in the above described NH_3-SO_2 tubes. These colored species have been observed before,[35] but neither their composition nor structure is conclusively known. Apparently, several singly charged radical ions, such as S_3^-, S_4^- and NS_4^- might be present. Astonishingly, ^{34}S does not yield the large expected shift. The color is also similar to that observed in molten salt, ultramarines and solutions of sulfides in

TABLE III

Raman spectra in blue solutions[a]

$NH_3 \cdot SO_2$	$NH_3 \cdot S_8$	S_x^- (ref. 35)	DMA + $Na_2S_{4.5}$ (ref. 36)	Color	Assignment
			235	blue	S_3^-, ν_2
		355		blue	NS_4^-,
			384	red	S_4^-, ν_x
400[b]	400[b]			purple	
			439	red	S_4^-, ν_y
450[b]	450[b]			purple	
519	519		518	red	S_4^-, ν_z
		535-543	535	blue	S_3^-, ν_1
580	584	580	586	violet	S_2^-, ν_1
		585		blue	NS_4^-
(709)	709[c]			purple	S-N
			768	blue	S_3^-, $\nu_1 + \nu_2$
		898		blue	NS_4^-

[a] Frequencies are average values. Combination bands above 800 cm^{-1} are not listed.

[b] Broad bands.

[c] Isotope shifts: D: -1.5 cm^{-1}, S: -8 cm^{-1}, N: -16 cm^{-1}.

organic amines. In these systems the presence of S_2^-, S_3^- and S_4^- have been documented by their characteristic ESR, UV and Raman spectra.[35] These ions are calculated to be quite stable.[39,40] To judge from ultramarines which contain similar ions, these systems can be indefinitely stable. A more complete discussion of these free radical systems goes beyond the scope of this paper.

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