N'-Sulfides. Dinitrogen Sulfide, Thiofulminic Acid, and Nitrile Sulfides

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I. Introduction

Whereas N-oxides (nitrones, nitrile oxides) are well-known compounds showing 1,3-dipolar reactivity,1 the corresponding N-sulfides are extremely unstable and short-lived under usual reaction conditions. N₂O is a particularly stable and unreactive molecule. N₂S, in contrast, is a reactive intermediate which only recently has yielded to direct spectroscopic detection. Fulminic acid (HCNO) and the nitrile oxides2 are reactive but nonetheless isolable compounds with a long history which in the case of the metal fulminates goes back to the alchemists.3 The nitrile sulfides have been known as reactive intermediates for only 20 years, and definitive spectroscopic characterization has been achieved only very recently. The HCNO isomers are interesting enough4 but in the sulfur series only iso-thiocyanic acid, HNCS, has been known until this year. HNCS has been identified in the interstellar cloud Sagittarius B2,6 and since some other sulfur containing species (C₂S and C₃S) show remarkably high abundances in the cold dark cloud TMC-1,6 one might expect to find the other HCNS isomers as well. Recent advances in the laboratory detection of elusive sulfur containing species7 including that of thiofulminic acid, HCNS (described below), leave little doubt that the missing isomers (HSCN and HSNC) will also eventually be made.

A review focusing on the chemistry of nitrile sulfides by R. M. Paton was published in 1989.8 The present review will emphasize mechanistic and spectroscopic aspects.

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II. Dinitrogen Sulfide, \( \text{N}_2\text{S} \)

A. Background

Powell\(^7\) attributed the carrier of an \( \text{N}_2\text{-CS}_2 \) laser to the linear NNS molecule. It was considered stable and unreactive at room temperature, showing no reaction with charcoal, soda lime, or steel wool, and passing freely through pump oil. It was further considered to be a byproduct of the combustion of coal. It is now known that \( \text{N}_2\text{S} \) is an extremely short-lived molecule, showing no reaction at room temperature, giving decafluoro diphenyl disulfide in high yield at 90-100 °C.\(^{22,23} \) On UV photolysis, a small amount (5-10%) of phenyl isothiocyanate is also formed.\(^{22} \) The nitrile forming reaction has usually been formulated as a concerted cycloreversion process, yielding sulfur atoms initially.\(^{20-24} \)

\[
\text{R}_2\text{PN}_5\text{S}_3 \rightsquigarrow \text{R-CN} + \text{N}_2 + \text{S}
\]

5-Substituted 1,2,3,4-thiatriazoles\(^{20,21} \) are thermally unstable, decomposing in some cases even at room temperature and sometimes with detonation.\(^{20} \) 5-Benzylthiatriazole decomposes to benzyl cyanide at room temperature, and the 5-phenyl derivative (5, \( \text{R} = \text{C}_6\text{H}_5 \)) affords benzonitrile, nitrogen, and sulfur in high yield at 90-100 °C.\(^{22,23} \) On UV photolysis, a small amount (5-10%) of phenyl isothiocyanate is also formed.\(^{22} \) The nitrile forming reaction has usually been formulated as a concerted cycloreversion process, yielding sulfur atoms initially.\(^{20-24} \)

Jensen, Burmester, and Bak (JBB)\(^{25} \) studied the kinetics of a series of 5-alkoxythiatriazoles (6) in dibutyl phthalate solution and found the reactions to be of first order with very little substituent dependence on the rate. The activation energies were all of the order of 24.6 kcal/mol, and the activation entropies 3.2-4.7 cal/mol K. They considered it plausible that the first step in the reaction involved S-N bond cleavage with the formation of a thio azide, which subsequently (and rapidly) eliminates nitrogen and sulfur, perhaps via a thioacylnitrene intermediate. Attempts to detect the thio azide by IR spectroscopy (expected at ca. 2130 cm\(^{-1} \)) were negative.\(^{26} \) The reaction constitutes a versatile synthesis of alkyl and aryl cyanates.\(^{26} \)

A thorough analysis of the thermal decomposition of 5-phenylthiatriazole (7) was carried out by Holm et al.\(^{27} \) The activation energy and entropy, measured for the first-order reactions in bromobenzene at 52-61 °C, were 28.2 kcal/mol and 2.8 cal/mol K, respectively. Four possible pathways, A-D, were considered (Scheme 1). Paths A and B both involve rate-determining \( \text{N}_2 \) loss, and since no kinetic isotope effect was observed for the
SCHEME I

\[
\text{PhCN} + N_2 \xrightarrow{k_2} \text{Ph-CN-S-S-Ph} \xrightarrow{k_1} \text{PhCN} + N_2S
\]

2-^{15}N isotopomer of 7, both of these routes were excluded.

The kinetic isotope effect for the 4-^{15}N isotopomer was \(\sim 4\%\), demonstrating that \(N_3-N_4\) bond breaking is very significant in the transition state. This would be in agreement with either paths C or D, but a search for \(N_2S\) (path C) by mass spectrometry was negative. It was concluded that \(N_2S\) was not formed, and, in agreement with JBB,\(^{29}\) pathway D was deemed the only route consonant with the experimental observations. The facts that no thiobenzyol azide was observable and that only one peak was observed in the differential thermogram required both \(k_1\) and \(k_2 \gg k_1\). CNDO calculations were in agreement with the expectation that the stable thiatriazole is of lower energy than the thiocarbonyl azide.\(^{28}\)

It must be pointed out here that the rejection of path C was based essentially on the inability to detect \(N_2S\), and on the erroneous belief of Powell\(^{9}\) that \(N_2S\) would be long-lived. As shown below, path C is indeed operating, and this reaction is a very convenient source of \(N_2S\). Thiobenzyol azide (8), in contrast, remains unknown.

C. Spectroscopy of \(N_2S\)

\(N_2S\) is produced by flash vacuum pyrolysis of 5-phenyl-1,2,3,4-thiatriazole (7) at temperatures between 300 and 750 °C (10^{-3}-10^{-6} Torr).\(^{29}\) The yield of \(N_2S\), qualitatively measured by its infrared absorbance relative to that of benzonitrile, critically depends on the contact time in the oven and hence on the oven design. \(N_2S\) is stable at 77 K and can be isolated as a neat solid. Thiobenzyl azide is of lower energy than the thiocarbonyl azide.\(^{28}\)

With the pyrolysis apparatus currently in use, the starting material 7 is completely consumed at a pyrolysis temperature well below 700 °C, and absorbance ratios, \(N_2S:PhCN\), as high as 15:1 can be obtained under these conditions. This means that the IR spectrum shows essentially a single, strong line at 2039 cm^{-1}, with a number of much weaker bands which can all be assigned to benzonitrile. With longer contact times, lower oven temperatures will suffice to achieve complete decomposition of 7, but \(N_2S\) will also in part decompose to \(N_2\) and sulfur under such conditions.\(^{29}\)

Once isolated, solid \(N_2S\) is stable until 160 K, when the 2039 cm^{-1} absorption disappears, the sample turns opaque, and sulfur is visibly formed. After the sample is warmed to room temperature, benzonitrile and sulfur are isolable in nearly quantitative yields.

The事实 that no thiobenzyl azide was observable and that only one peak was observed in the differential thermogram required both \(k_1\) and \(k_2 \gg k_1\). CNDO calculations were in agreement with the expectation that the stable thiatriazole is of lower energy than the thiocarbonyl azide.\(^{28}\)

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Ab initio calculations using the HF/6-31G* basis set predict a linear structure of NNS with \(R_{NN} = 1.086 \text{ Å}\) and \(R_{NS} = 1.652 \text{ Å}\). The predicted stretching fundamentals are \(\nu_{NN} = 2602 \text{ cm}^{-1}\) and \(\nu_{NS} = 583 \text{ cm}^{-1}\). Since the 6-31G* basis set typically overestimates vibrational frequencies by a factor 1.12, the observed \(\nu_{NN}\) frequency of 2039 cm^{-1} is somewhat lower than predicted by theory. The \(\nu_{NS}\) stretching band, predicted at 583 cm^{-1} and due essentially to an N-S single bond, may similarly be expected in the vicinity of 400 cm^{-1}. This band has not as yet been located experimentally, but all the spectra of \(N_2S\) from 7, 9, and 10 feature a second, very weak band at 752 cm^{-1} which shows the same thermal and photochemical behavior as the strong 2039 cm^{-1} band. Both bands are bleached by irradiation with 254 nm light (8-10 h at 10 K). A possible interpretation of the 752 cm^{-1} feature is \(2\nu_{NS}\). Current instrumentation does not allow us to observe \(\nu_{NS}\) itself.

Subsequent to the matrix isolation work\(^{29}\) Brown et al.\(^{31}\) used our method to record the high-resolution gas-phase IR spectrum of \(N_2S\), produced by thermolysis of 7 at 300 °C. The transient \(N_2S\) was detectable only by allowing the pyrolyzate to flow through the 16-m pathlength multiple reflection cell at the maximum pumping capacity of the system. With less-efficient pumping and hence longer contact times, only a broad, featureless absorption due to a stable and unknown molecule was observed; this absorption (2047 cm^{-1}) is evidently not due to \(N_2S\) but very likely to a trace of phenyl isothiocyanate, a known byproduct, which absorbs strongly around 2050 cm^{-1} in the gas phase and at 2047 cm^{-1} in matrix. The \(\nu_{NN}\) stretching fundamental (\(\nu_9\)) of the transient \(N_2S\) gas phase species was observed at 2047.59 cm^{-1}.

Analysis of the fine structure of this band due to the \(N_2S^{24}\)S and \(N_2S^{32}\)S isotopomers afforded the rotational and centrifugal distortion constants and the bond lengths \(R_{NN} = 1.1388 \text{ Å}\) and \(R_{NS} = 1.5775 \text{ Å}\) in good agreement with MP3/6-31G* calculations. From the equilibrium B value, the N-S bending frequency (\(\nu_9\)) was calculated as 343 cm^{-1}. Neither \(\nu_9\) nor the \(\nu_{NS}\) stretching vibration (\(\nu_8\)) were observed directly, and their calculated intensities were significantly less than that of \(\nu_9\) at 2047 cm^{-1}. 
The high-resolution gas-phase IR spectrum proves the structure of N₂S beyond doubt. The composition was also proved by pyrolysis—mass spectrometry. The molecular ion of H₂N₂ almost vanished at 240 °C, whereas that of N₂S (m/z 60) increased in intensity, and its composition was confirmed by high-resolution mass measurement. Interestingly, S₂ is also a pyrolysis product, as seen both in the mass spectrum and the photoelectron spectra.

The photoelectron spectrum of N₂S was obtained by pyrolysis of 7 at 310 °C with computer subtraction of bands due to benzonitrile and N₂. The data are summarized in Table I, and the first ionization potentials of the diazonium betaines are compared in Table II. The ionization data for N₂S indicate a relatively weak N—S interaction in the linear N₂S molecule, in agreement with the long N—S bond. The ionization potential as well as the infrared frequency indicate that N₂S is more closely related to CH₂N₂ than to the stable and unreactive N₂O. Peaks due to benzonitrile and NPN were also clearly observed in the spectra, but monatomic sulfur was absent. The temperature dependence of the intensities of N₂S and S₂ peaks indicates that S₂ is a secondary product, arising from N₂S decomposition.

Therefore, the reaction, N₂S → N₂ + S can be excluded. Two possible mechanisms for S₂ production are given in eqs 2–3.

\[
\begin{align*}
2\text{N}_2\text{S} & \rightarrow \text{N}=\text{S} \cdots \text{S} \cdots \text{N}=\text{N} \rightarrow 2\text{N}_2 + \text{S}_2 \quad (2) \\
2\text{N}_2\text{S} & \rightarrow \text{N}:=\text{N} \cdots \text{S} \cdots \text{N} &= \text{N} \rightarrow 2\text{N}_2 + \text{S}_2 \quad (3)
\end{align*}
\]

Weak signals due to traces of PhNCS were visible in both the infrared, the mass, and the photoelectron spectra, in agreement with the observations of Kirmse and Holm. Photolysis of 7 in an Ar matrix also produces N₂S and benzonitrile as observed by IR spectroscopy. The photoreaction is very slow at 310 nm; it was faster at 254 nm, but prolonged irradiation at this wavelength destroys N₂S. The photoreaction is accompanied by traces of phenyl isothiocyanate.

In summary, the ensemble of spectroscopic properties conclusively proves the identity of N₂S. It is a linear molecule with a rather weak N—S bond. The transient nature of N₂S is not due to inherent thermodynamic instability, however, for there is no evidence for decomposition into N₂ and S₁. The molecule decomposes primarily in a bimolecular process yielding N₂ and S₂. Therefore, high-vacuum and/or low-temperature methods are required to preserve the molecule.

### III. Thiofulminic Acid, H—C≡N—S

#### A. Background

Of the four theoretically possible HCNS isomers, only one, isothiocyanic acid HNCS, was previously known. Ab initio calculations indicate that thiofulminic acid, H—C≡N—S, is a linear molecule. It is also the highest energy isomer, in contrast to the HCNO isomers, where isofulminic acid, H—N—C═N, is the least stable. The energy orderings are illustrated in Figure 1. HONC and its esters, R—O—NC, have recently been characterized by matrix isolation techniques.

Calculations using the 6–31G* basis set further indicate that CNS and NCS radicals and anions occupy energy minima and that the energy difference between the two is substantially lower than for the CNO/NCO analogues, both in the neutral and the anionic series. Vibrational frequencies for the thiofulminate anion, CNS−, have been calculated; at the Møller–Plesset/2 level, \( \nu_1 = 570; \nu_2 = 321; \nu_3 = 2109 \text{ cm}^{-1} \).

It is believed that substances containing thiofulminate ligands are formed in the reaction between potassium hexacyanoferrate(III) and molten sulfur at 200 °C. This interpretation is due largely to infrared spectroscopy, the compounds showing very strong absorptions at 2071–2025 cm⁻¹. However, the assignment of strong bands at 1215–1108 cm⁻¹ to the N—S stretching vibration on the basis of analogy with the N—O stretch at 1205–1050 cm⁻¹ in fulminate ligands seems dubious and is in disaccord with the above calculations for the thiofulminate anion.

#### B. Detection of Thiofulminic Acid

Attempts by Bak et al. to observe HCNS by pyrolysis and photolysis of 1,3,4-oxathiazol-2-one (12) were not encouraging.

Only isothiocyanic acid (HNCS), CO₂, and HCN were observed by microwave and mass spectrometry in the thermal process (700 °C, 2.10⁻² Torr), and HCN, CO₂, OCS, and HNCO in the photochemical process. The same products were obtained on gas-phase irradiation.
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with a CO₂ laser operating at 10.5 μm.⁵²

\[
\begin{align*}
\text{HCSN} & \rightarrow \text{HCS} + \text{HCN} + \text{CO}_2 \\
\text{HNCS} + \text{CO}_2 & \rightarrow \text{HNCO} + \text{N}_2
\end{align*}
\]

Nevertheless, we have used 12 to obtain the first direct evidence for the existence of neutral H—C=S—N by using neutralization—reionization mass spectrometry (NRMS).⁵⁷ In this technique, a beam of mass-selected ions is neutralized in a collision cell by colliding it with Xe and then reionized in a second collision cell by collision with O₂. The recovery of a mass spectrum of the resulting ions implies the existence of the corresponding neutral molecules with lifetimes of the order of at least 0.5 μs.

The collision—activation mass spectrum (CAMS) of isothiocyanic acid (HNCS) is characterized by signals at m/z 27 (HCN), 32 (S), and 44 (CS). The CAMS of the mass-selected m/z 59 ions (M — CO₂) emanating from the electron ionization (EI) mass spectrum of oxathiazolone 12 also shows signals at m/z 27 and 32, but differs from that of HNCS by an intense peak at m/z 46 (NS). This clear differentiation demonstrates that the m/z 59 ion formed by fragmentation of 12⁺ has the structure H—C=N—S⁺.

The NRMS of H—N==C==S⁺ regenerates, as expected, a mass spectrum identical with the original CAMS of this ion. The NRMS of the m/z 59 ions from 12⁺ likewise regenerates a strong survivor signal at m/z 59, with a spectrum identical with the original one, and in particular still showing the characteristic m/z 46 (NS) signal. Thus, neutral H—C=N==S does not isomerize to H—N==C==S to any significant extent on the microsecond time scale of this experiment.³⁷

IV. Nitrile Sulfides, RCNS

A. Generation and Trapping Reactions

1. From 1,3,4-Oxathiazol-2-ones

Benzonitrile sulfide was first generated by Franz and Black³⁸ by thermolysis of 4-phenyl-1,3,4-oxathiazol-2-one (13) in chlorobenzene at 130 °C and trapped in a 1,3-dipolar cycloaddition reaction with dimethyl acetylenedicarboxylate in over 90% yield.

\[
\begin{align*}
\text{Ph} & \rightarrow \text{Ph} \\
\text{HCN} & \rightarrow \text{HCN} \\
\text{CO}_2 & \rightarrow \text{CO}_2
\end{align*}
\]

Oxathiazolones of the type 13 had first been prepared by Senning³⁹ and by Muhlbauer and Weiss,⁴⁰ and Senning had noted that "pyrolysis" resulted in the nitrile, CO₂, and sulfur. This is a common observation: in the absence of a dipolarophile, or with inefficient dipolarophiles, the nitrile sulfide decomposes to the nitrile and sulfur. As in the case of N₂S, we do not expect this to be a unimolecular process with monomolecular sulfur formation:

\[
\text{R—C==N—S} \rightarrow \text{R—C==N} + "S"
\]

We shall return to this point in section C.

Kinetic studies of the reaction shown in eq 5 were in agreement with rate-determining formation of the nitrile sulfide intermediate and excluded the possibility of a direct reaction between 13 and the trapping agent.⁴¹

In further work, nitrile sulfides have been added to a variety of electron poor acetylenes,⁴²,⁴³ electron poor or strained (norbornene) alkenes,⁴⁴,⁴⁵ and to the CC double bond in p-quinones.⁴⁶ Intramolecular addition to electrophilic CC triple bonds also occurs with formation of bicyclic isothiazoles in good yields.⁴⁷ Intramolecular addition to CC double bonds is less efficient and results in secondary reactions.⁴⁷ The addition to CC multiple bonds has been utilized in the modification of unsaturated polymers by cross-linking with arylene bis(nitrile sulfides)⁴⁸ and in the production of polymers from copolymer-bound oxathiazolones which on heating generate nitrile sulfides that can be trapped with dimethyl acetylenedicarboxylate, ethyl propiolate, diethyl fumarate, etc.⁴⁹

Aromatic nitrile sulfides add efficiently to the CN triple bond in electrophilic nitriles such as ethyl cyanoformate,⁵⁰,⁵¹ aromatic nitriles,⁵²,⁵³ trichloroacetanilide,⁵⁴ and acyl cyanides⁵⁵ and in aryl thiocyanates and selenocyanates.⁵⁶ Likewise, addition takes place to the CN group in tetracyanoethylene and not to the CC double bond.⁵⁷ Benzonitrile sulfide also adds to the CP triple bond in tert-butylphosphoracetylene to give a 1,2,4-thiazaphosphole in 82% yield.⁵⁸

Reaction with imines (Schiff's bases of aromatic aldehydes) gives only poor yields of cycloadducts.⁵⁹ Perhaps more electrophilic imines should be investigated. Cycloaddition with electrophilically substituted aldehydes and ketones, such as chloral, hexachloroacetone, and trifluoroacetophenone yields 1,3,4-oxathiazoles in modest to good yields.⁶⁰

1,4,2-Dithiazoles are similarly obtained in 10—65% yield by cycloaddition to the CS double bond in alkyl aryl thioketones and in O-ethyl thiobenzoate.⁶¹

The various reaction types are illustrated in Scheme II and further preparative details are given in Paton's review.⁵ It is usually advantageous to add the ox-
thiazolone precursor slowly to the hot solution of the
dipolarophile in order to maintain a low concentration of
nitrile sulfide and a high reaction temperature.
Yields are increased by low solvent polarity, for example
by adding dodecane as a diluent. While most studies have
been carried out with aromatic nitrile sulfides, also
alkyl (e.g. CH₃CNS, tert-C₄H₉CNS), vinyl dimethylamino
(Me₂N-CNS), and 5-β-D-ribofuranosyl substituents have been
employed.

It is a general observation that these cycloadditions
are favored by electropositive substituents in the nitrile
sulfide and by electronegative ones in the dipolarophile.
In other words, the reactions are dominated by HOMO
(dipole) – LUMO (dipolarophile) interaction. In this
regard, the nitrile sulfides are more closely related to
nitrile ylides than to nitriles imines or nitrile oxides.

3. From 1,3,4-Dithiazol-2-ones

The dithiazolones 15 are more stable than oxathia-
zolones 13 but decompose to nitrile sulfides in boiling
mesitylene (160 °C). The nitrile sulfides (R = CH₃ or
C₆H₅) were trapped with dimethyl acetylenedicarboxylate in 56
and 52% yields, respectively.

The corresponding dithiazolethiones 17 give low
yields of 16 on photolysis, but the thermal reaction
takes a different course, and thus 17 is not a prepara-
tively useful nitrile sulfide source.

4. From 1,3,2-Oxathiazolo 5-Oxides

Gotthardt found that solution photolysis (450-W
medium-pressure Hg lamp; λ > 395 nm or λ = 405-408
nm) of 4-aryl-1,3,2-oxathiazolo 5-oxides 23 in the
presence of dimethyl acetylenedicarboxylate led to
nitrile sulfide cycloadducts 26 in yields varying from 0
to 31%. Tetramethyl thiophenetetracarboxylate was
formed as well and is a known product of reaction of
the acetylene with elemental sulfur. In the absence
of a trapping agent, benzonitrile (77%) and sulfur (>90%)
were obtained from the 4-phenyl compound. It was
suggested that the thiazirine 24 and the nitrile sulfide
25 were reactive intermediates.

The thermal reaction between 23 and acetylene dicarboxylate at 85-95 °C took a different course, in-
volving direct cycloaddition to 23 followed by CO₂
elimination to give the isomeric isothiazole 27.71

However, the thermal reaction of 28 with tert-bu-
tylphosphacetylene in benzene solution at 80 °C has
been reported to give a 1:9 mixture of the isomeric cycloadducts 29 and 30, thereby indicating that nitrile sulfide formation from 28 can also take place thermally.\textsuperscript{72}

\[
\begin{array}{c}
\text{Ph} & \text{N} + \text{C} & \text{P} \\
\text{28} & \text{28} & \text{28}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} & \text{N} & \text{S} & \text{Ph} \\
\text{29} & \text{29} & \text{29}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} & \text{N} & \text{S} & \text{Ph} \\
\text{30} & \text{30} & \text{30}
\end{array}
\]

5. From N-(Thiocarbonyl)-S,S-diphenylsulfimides

An interesting reaction is reported for the sulfimides 31 which, at temperatures as low as 70 °C decompose to nitrile and sulfur, and in the presence of dimethyl acetylenedicarboxylate give the expected trapping product of a nitrile sulfide 32. Analogous products were obtained with other alkynes.\textsuperscript{73a} The combined yield of nitrile and 32 was quantitative. The reaction was first order, and the rate of appearance of the nitrile was independent of the presence or absence of the alkyne, and also the rate of appearance of 32 was independent of the alkyne concentration but highly dependent on the electrophilicity of the alkyne. It was assumed that the nitrile sulfide was in rapid equilibrium with the thiazirine and that the latter was the source of ArCN and sulfur. This is in disagreement with other work, which has demonstrated sulfur loss from nitrile sulfides and sulfur. This is in disagreement with other work, \textsuperscript{73b} The reaction seems worthy of further investigation.

\[
\begin{array}{c}
\text{Ph} & \text{S} & \text{N} & \text{N} & \text{Ph} \\
\text{31} & \text{31} & \text{31}
\end{array}
\]

\[
\begin{array}{c}
\text{Ar-CN} \\
\text{32}
\end{array}
\]

6. From (Alkylimino)sulfur Difluorides

Aromatic and aliphatic nitrile sulfides have been generated by fluoride ion induced HF elimination from iminosulfur difluorides.\textsuperscript{83} The nitrile sulfides have been trapped with acetylenic esters and by addition to the CC double bond in quinones and in N-phenylmaleimide.\textsuperscript{53,74}

\[
\begin{array}{c}
\text{R-CH} & \text{N} & \text{S} & \text{F}_2 \\
\text{33} & \text{33} & \text{33}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} & \text{N} & \text{S} & \text{Ph} \\
\text{7} & \text{7} & \text{7}
\end{array}
\]

7. From Thioamides and Related Compounds

Nitrile sulfides have been invoked in a variety of oxidative reactions of aromatic thioamides.\textsuperscript{75-76} In most cases there is little or no decisive evidence for the actual involvement of a nitrile sulfide, and in at least one case the nitrile sulfide was deemed not to be involved.\textsuperscript{77}

It has also been suggested\textsuperscript{76} that nitrile sulfides may be involved in the formation of so-called abnormal products (cyanoalkyl episulfides) of catabolism of glucosinolate anions (thiohydroximate O-sulfonates).

\[
\begin{array}{c}
\text{Ph} & \text{N} & \text{S} & \text{Ph} \\
\text{36} & \text{36} & \text{36}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} & \text{C} & \text{O} & \text{O} & \text{Et} \\
\text{35}
\end{array}
\]

B. Direct Observation

1. UV Spectroscopy

Holm et al.\textsuperscript{79} examined the photolysis of 4-phenyl 1,3,2-oxathiazolo 5-oxide (28) in an EPA glass at 85 K by UV spectroscopy. Irradiation with 420 ± 13 nm light caused the appearance of two intermediates, assigned as the ketene (\(\lambda_{\text{max}} 324 \text{ nm}\)) and benzonitrile sulfide (37) (\(\lambda_{\text{max}} 355, 313, 295, 240 \text{ nm}\)) (Scheme III). Irradiation with 335 ± 14 nm light caused disappearance of these intermediates, whereby 34 disappeared more slowly. 34 was trapped in separate experiments by photolysis in ethanol solution, giving a 65% yield of ethyl phenyglyoxylate (35) together with 21% of benzonitrile.\textsuperscript{79,80} Warming of the EPA glass containing 34 and 37 to room temperature also resulted in benzonitrile formation.\textsuperscript{79} The EPA glass at 77 K did not contain any radicals according to ESR spectroscopy, but prolonged irradiation at 335 nm caused appearance of an ESR signal ascribed to an RS' radical, presumably the thiyl formed by NO elimination from 34.\textsuperscript{79,81}

It was subsequently found that the same UV absorptions ascribed to benzonitrile sulfide (37) were also generated by photolysis of both phenylthiatriazole (7) and phenyloxathiazolone (13) in EPA glass at 85 K.\textsuperscript{82} Room temperature photolysis in the presence of dimethyl acetylenedicarboxylate resulted in a 9% yield of cycloadduct from 7, and 22% from 13. Thus, re-

\[
\begin{array}{c}
\text{Ph} & \text{N} & \text{S} & \text{Ph} \\
\text{36}
\end{array}
\]

markably, at least some nitrile sulfide 37 is formed on photolysis of 7, whereas the thermal reaction gives largely N\_2S (section II). Ar matrix photolysis of 7 also gives N\_2S albeit in small amount (section II) and no PhCNS, and liquid-phase photolysis gives phenyl isothiocyanate in ca. 7% yield.\textsuperscript{22,82}

In spite of the complexities, it seems clear that 37 is formed, and the reaction is assumed to occur via the thiazirine 36. No ESR active species such as thio-benzylnitrene was detectable.

Evidence for the initial formation of thiazirine 36 as a common intermediate was adduced from photolysis of several precursors (Scheme IV) in PVC film at 10-15 K.\textsuperscript{83} Although no discrete UV bands could be assigned
to the low-temperature intermediate, warming of the samples from 20 to 145 K resulted in the appearance of the UV spectrum of benzonitrile sulfide (37), the absorptions growing in a stepwise fashion (Scheme IV). The UV spectrum of 37 can be observed in the PVC film even after warming to room temperature. The dithiazolethione 17 (R = C6H5) did not, however, give any benzonitrile sulfide on such treatment. All the precursors in Scheme IV as well as thione 17 and several other heterocyclic compounds afforded the nitrile sulfide cycloaddition product with dimethyl acetylenedicarboxylate in yields of 5–21% on liquid-phase photolysis at room temperature.68

2. IR Spectroscopy

The observations made by UV spectroscopy have been correlated with IR spectroscopy in N2 matrix and in PVC film.61 Broadly, the mechanism given in Scheme III is confirmed. The nitrosothio ketene 34 absorbs at 2100 cm⁻¹ in PVC film and at 2115 cm⁻¹ in N2 matrix. It is in photoequilibrium with the starting material 28, exists in Z and E forms, and on further photolysis is cleaved into a thyl radical.

The nitrile sulfide 37 is not observed in N2 matrix, but in PVC film at 80–85 K it absorbs at 2185 cm⁻¹. 37 is formed by irradiation of the precursor 28 in the film at 470 nm, i.e. the edge of the absorption band, and it appears before bands due to benzonitrile. 37 is bleached by photolysis into its UV maximum at 335 nm. Warmup caused 37 to disappear at ca. -60 °C (but being observable up to room temperature in PVC under certain conditions), and the temperature profile for disappearance was the same as that established by UV spectroscopy.

No other valence tautomer of the oxathiazole 5-oxide 28 was observed by IR (or UV) spectroscopy, nor was thiazirine 36 apparent in the IR (or UV) spectra.

While these studies established the existence and properties of benzonitrile sulfide without doubt, there still was no direct evidence for nitrile sulfides in thermal reactions, especially in the preparatively most versatile thermolyses of oxathiazolones and oxathiazoles (eqs 5 and 7).

We therefore embarked on an Ar matrix isolation study of the flash vacuum pyrolysis products of the precursors 13, 38, and 39 (Scheme V).62,64 Pyrolysis of 13 at 550 °C with Ar matrix isolation at 20 K produced CO2, benzonitrile, and a species absorbing at 2185 cm⁻¹.

Since 37 decomposes thermally to benzonitrile and sulfur, it is not possible to obtain a large amount of 37 in this way. The best ratio of the absorbances of benzonitrile and 37 was 3.6:1. Photolysis of this matrix with 335-nm light caused disappearance of the 2185 cm⁻¹ absorption with a concomitant slight increase in the benzonitrile absorption clearly seen in the difference spectrum. The hexachloroacetone derivative 38 was an even better precursor of benzonitrile sulfide under identical conditions, and again the 2185 cm⁻¹ species was bleached with 335 nm light. Careful evaporation of the Ar at >50 K also caused the 2185 cm⁻¹ peak to vanish. The chloral derivative 39 was a poorer precursor of 37, giving a weak signal at 2185 cm⁻¹ together with benzonitrile, chloral, and dichloro ketene.

These results make it clear that benzonitrile sulfide is a discrete intermediate in both the photochemical and the thermal processes. It is perhaps a priori surprising that it survives flash pyrolyses at temperatures above 500 °C, although the yield of the trapped nitrile sulfide is definitely low. Further proof of the identity of the gas-phase species was obtained by mass spectrometry.37 Acetonitrile sulfide, CH3-C≡N-S, was identified by IR spectroscopy in a similar manner (2230 cm⁻¹). The higher frequency vis-a-vis Ph-C≡N-S is in accord with the higher frequencies of CH3NCS, CH3SCN, and CH2CN with respect to the phenyl analogues. The 2230 cm⁻¹ species was again bleached by short wavelength light. The proof of its composition was given by mass spectrometry (see below).

3. Mass Spectrometry

The EI mass spectrum of 13 shows the molecular ion (m/z 179), a weak signal corresponding to benzonitrile sulfide (m/z 135), and a weak one due to benzonitrile (m/z 103). The base peak is m/z 105, corresponding to PhCO+. Pyrolysis above 200 °C causes the molecular ion and PhCO⁺ to disappear, and the benzonitrile ion becomes the base peak. CO₂ appears at the same time, and there is a small increase in the signal due to S₂ at m/z 64, whose composition was determined by high-resolution mass measurement. There was no definite increase in the already weak signal due to PhCNO at m/z 135, indicating that PhCNO may decompose thermally at a rate similar to that of its formation. This ion was still detectable at 500 °C, however.65

The hexachloroacetone derivative 38 again proved to be the best thermal precursor. Although the intensity of the m/z 135 ion (PhCNS) decreased over the temperature range 100–500 °C, the intensity decrease was less rapid above 270 °C, and from 300 °C onward this
signal became relatively stronger than those due to the rapidly disappearing starting material 38. The signal due to S₂ increased over the whole temperature range, and benzonitrile (m/z 103) became the base peak from 220 °C onward.

The identity of the m/z 135 ion as the molecular ion of benzonitrile sulfide (37) was established for several different precursors (Scheme VI) by using kinetic energy, metastable ion, collision activation (CA), and neutralization-reionization (NR) mass spectrometry. In particular, the CA spectrum of 37 is characterized by a very strong loss of S₄.

The molecular ion of Ph-C≡N-S⁻ (m/z 135) is readily distinguished from those of Ph-N≡C-S and Ph-S-C≡N (Table III). Note that the m/z 135 ion from phenylthiatriazole (7) is due to Ph-N⁻C≡S⁺, not Ph⁻C≡N⁻S⁺ (Scheme VI).

The proof that the neutral Ph-C≡N-S⁻ (37) also exists in the gas phase and has the same structure as the ion Ph⁻C≡N⁻S⁺² was given by NRMS of m/z 135 produced from 13 and 40. These spectra clearly showed survivor signals at m/z 135, with the characteristic sulfur loss to give m/z 103,82

In like manner, acetonitrile sulfide was observed by matrix isolation IR spectroscopy at 2230 cm⁻¹ as formed by flash vacuum pyrolysis of 42 at 300–500 °C. The oxathiazole 43 gave no comparable signal under similar conditions.87

**TABLE III. Collision Activation Mass Spectra of m/z 135 C₆H₅NS⁻⁺ Ions**

<table>
<thead>
<tr>
<th>precursors</th>
<th>108 (340)</th>
<th>103 (90)</th>
<th>91 (200)</th>
<th>90 (157)</th>
<th>84 (488)</th>
<th>82 (129)</th>
<th>77 (43)</th>
<th>76 (14)</th>
<th>69 (15)</th>
<th>63 (11)</th>
<th>58 (8)</th>
<th>51 (10)</th>
<th>50 (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>64 (17)</td>
<td>30 (15)</td>
<td>17 (1140)</td>
<td>22</td>
<td>15</td>
<td>35</td>
<td>5</td>
<td>100</td>
<td>52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td>45 (18)</td>
<td>15 (356)</td>
<td>100</td>
<td>16</td>
<td>32</td>
<td>5</td>
<td>52</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td></td>
<td></td>
<td>43 (14)</td>
<td>11 (310)</td>
<td>100</td>
<td>14</td>
<td>22</td>
<td>6</td>
<td>52</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td></td>
<td></td>
<td>40 (15)</td>
<td>8 (333)</td>
<td>100</td>
<td>11</td>
<td>28</td>
<td>4</td>
<td>50</td>
<td>41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td>10 (317)</td>
<td>100</td>
<td>11</td>
<td>27</td>
<td>4</td>
<td>47</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td></td>
<td></td>
<td>13 (720)</td>
<td>100</td>
<td>11</td>
<td>32</td>
<td>5</td>
<td>100</td>
<td>49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhNCS</td>
<td></td>
<td></td>
<td>17 (100)</td>
<td>11</td>
<td>28</td>
<td>4</td>
<td>50</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhSCN</td>
<td></td>
<td></td>
<td>13 (720)</td>
<td>100</td>
<td>11</td>
<td>27</td>
<td>4</td>
<td>47</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Abundances relative to the most intense collision induced peak excluding unimolecular processes which are noted in parentheses.

**SCHEME VI**

by flash vacuum pyrolysis of 42 at 300–500 °C. The oxathiazole 43 gave no comparable signal under similar conditions.87

The EI mass spectra of 42 and 43 also show abundant ions due to CH₅⁻C≡N⁻S⁻ (m/z 73) (100% in the case of 42; 10% in the case of 43). The structure CH₅⁻C≡N⁻S⁻⁺ was established by differentiation of the kinetic energy, metastable ion (MI), and CA mass spectra from those of the isomeric CH₅⁻N⁻C=⁻S⁻ and CH₅⁻S⁻⁻C=N⁻ ions. The CAMS of CH₅NCS⁻⁺ is characterized by a signal at m/z 44 (CS); that of CH₅SCN⁻⁺ by a loss of HCN (to m/z 46); and that of CH₅⁻C=⁻N⁻S⁻⁺ by signals due to NS and HNS (m/z 46, 47). Both CH₅NCS⁻⁺ and CH₅SCN⁻⁺ show strong losses of one hydrogen atom in the MI spectra, a fragmentation which is absent for CH₅⁻C≡N⁻S⁻⁺. Likewise, these ions have very different kinetic energy release profiles.87

Finally, NRMS with Xe/O₂ resulted in a survivor signal for CH₅⁻C≡N⁻S⁺, originally formed by dissociation of 43⁺. The NRMS of CH₅⁻C≡N⁻S⁻ showed the same characteristics as the CA spectrum and was again distinguishable from the NRMS of CH₅NCS and CH₅SCN. Thus, the existence of neutral CH₅⁻C≡N⁻S⁻ molecules with lifetimes of at least microseconds in the gas phase is established.87

**C. Mechanism of Sulfur Loss from Nitrile Sulfides**

As mentioned above, matrix-isolated aromatic nitrile sulfides usually decompose to the nitrile and sulfur on warming to ca. 140 K, except in the rigid PVC matrix, where they are observable for short periods at room temperature.82

It has long been realized that the liquid-phase decomposition of benzonitrile sulfide is not a simple unimolecular reaction.83,85,87 Howe and Shelton suggested that the decomposition is accelerated by reaction with short sulfur chains (S₁ to S₇), i.e. by a sulfur-transfer reaction. Holm et al. demonstrated pseudo-first-order decay rates in highly dilute (10⁻⁶–10⁻⁸ M)
ethanolic solutions at room temperature (lifetimes \( \sim 1 \) ms; \( E_u \sim 4.3 \) kcal/mol; \( \Delta S^* \sim 30 \) cal K\(^{-1}\)mol\(^{-1}\)). The decay rates were 3-4 times slower in a less polar solvent (CCl\(_4\)), and deviation from first-order kinetics was observed here. A direct involvement of ethanol in the transition state would give rise to the pseudo-first-order kinetics observed in that solvent. The sulfur was expected to be extruded initially as \( S \) atoms, but reactions between RCNS and \( S \), giving \( S_2 \), would cause higher-order kinetics, and this would be more dramatically evident in concentrated solutions.

If the activation energy for unimolecular decomposition was only ca. 4 kcal/mol, we would not expect to be able to matrix isolate nitrile sulfides formed in flash vacuum pyrolysis reactions.

In all the pyrolysis-mass spectrometry studies we see \( S_2 \) (m/z 64) increasing in intensity with the temperature. In the purely mass spectrometric unimolecular reactions, loss of atomic \( S \) is, of course, seen from the \( R-C=N-S^+ \) ions. In the case of CH\(_3\)-C=N-S\(^+\) produced from either \( 42^+ \) or \( 43^+ \) (Scheme VII), there is a very marked increase in the \( S_2 \) signal at the onset of pyrolysis (250-400 °C). At the same time, the molecular ions \( 42^+ \) and \( 43^+ \) disappear, and the \( S_2 \) signals (m/z 32) are greatly reduced as less acetonitrile sulfide arrives at the ion source due to thermal fragmentation.

Therefore, in analogy with the \( N_2S \) case (section II) we tentatively suggest \( S_2 \) formation via dimerization or (more likely) sulfur atom transfer mechanisms:

\[
2R-CNS \rightarrow [R-C=N-S-S-N=CR]^{-} \rightarrow 2RCN + S_2
\]

\[
2R-CNS \rightarrow [R-C=N-S-S-N=CR]^{+} + RCN \rightarrow 2RCN + S_2
\]

There are many other reactive sulfur species that may decay via sulfur atom transfer and \( S_2 \) formation, e.g. the thione \( S \)-sulfides reported by Huisgen et al.\(^{86}\) for which a mechanism is suggested in Scheme VIII. The powerful modern mass spectrometric techniques would seem to be best suited for investigations of such reactions in the gas phase. Solution-phase studies will be complicated by the instability of \( S_2 \) and other short sulfur chains.

**V. References**

3. (a) Mercury fulminate was prepared by C. Dreibel (1752-1763) and J. Kunkel von Löwenstern (1630-1703). The publication by Howard in the year 1800 was the first scientific description of this salt.\(^{b}\) (b) Kirmse, W.; Other, D. F. In Encyclopedia of Chemical Technology: Interscience Encyclopedia: New York, 1967; Vol. 6, p. 10. (c) Howard, E. Phil. Trans. Roy. Soc. London 1800, 204.