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THIOFULMINIC ACID (H–C≡N→S) AND NITRILE SULFIDES (R–C≡N→S) IN THE GAS PHASE

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Abstract. Thiofulminic acid (HCNS) and its derivatives have been identified in the gas phase by neutralization–reionization mass spectrometry, and benzonitrile sulfide also by matrix isolation IR spectroscopy following flash vacuum pyrolysis.

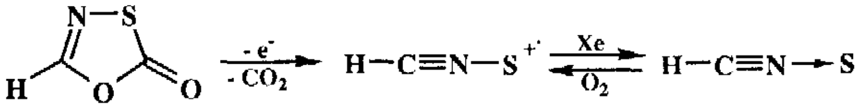
In contrast to the well–known *N*-oxides, the *N*-sulfides are short–lived reactive intermediates and our knowledge of the discrete molecules is very limited. Dinitrogen sulfide (N_2S) is a highly unstable molecule which has recently been characterized in the gas phase and in matrices.[3] Thiofulminic acid (HCNS) is unknown, and attempts to detect it in the gas phase or in matrices were unsuccessful.[4] Ab initio calculations indicate that the linear H–C≡N→S is the highest energy CHNS isomer, in contrast to the CHNO series where isofulminic acid, H–O–NC, is the least stable.[5]

In addition to the fundamental importance of identifying short–lived molecules and establishing their involvement in chemical reactions, there is also interstellar chemical interest in the species reported here. Isothiocyanic acid (HNCS), the only CHNS isomer known, has been identified in the interstellar cloud Sagittarius B2.[6] Other sulfur containing species (C_2S and C_3S) show remarkably high abundances in the cold dark cloud TMC–1.[7] It may be expected, therefore, that other HCNS isomers and carbon sulfides may be present as well.

Here we report the detection of thiofulminic acid in the gas phase.

In spite of previous unsuccessful attempts,[4] we have employed 1,3,4–oxathiazole–2–one (**1**) to obtain the first direct evidence for the existence of neutral HCNS using neutralization–reionization mass spectrometry (NRMS). In this technique[8] 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 with O_2. The recovery of a mass spectrum of the resulting ions implies the existence of the corresponding neutral molecules with life–times of the order of a microsecond.

The collision–activation mass spectrum (CAMS) of the m/z 59 ions generated by direct ionization of isothiocyanic acid (H–N=C=S) (Figure 1a) is characterized by signals at m/z 27 (HCN), 32 (S), and 44 (CS). The CAMS of the m/z 59 ions (M–CO_2) produced by electron ionization of **1** is remarkably different (Figure 1b): in place of the m/z 44 signal, there is a strong peak due to NS (m/z 46). Given



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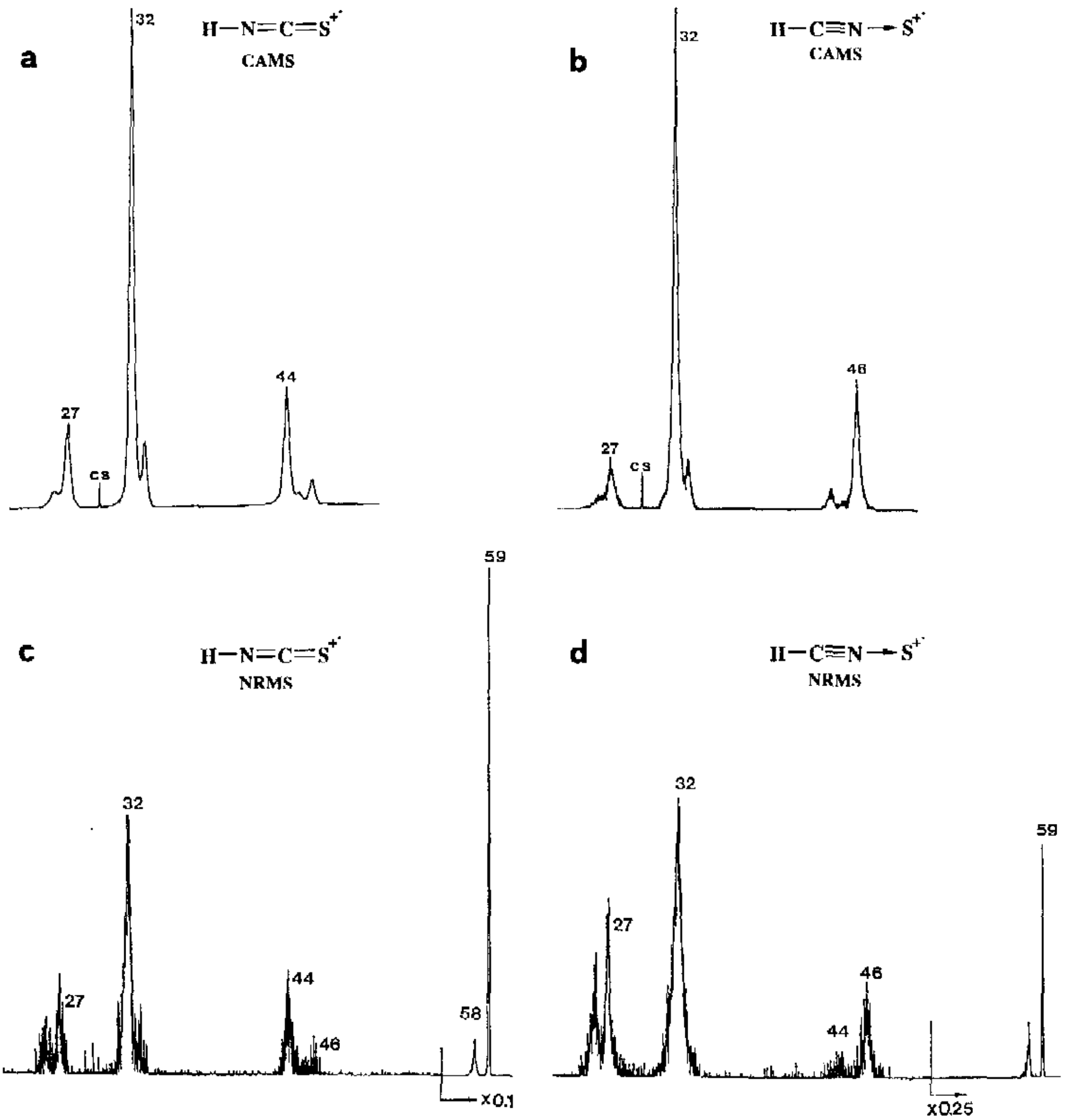


Figure 1. (a) CAMS of HNCS⁺; (b) CAMS of HCNS⁺; (c) NRMS of HNCS⁺; (d) NRMS of HCNS⁺·. CA spectra recorded on E/B/E spectrometer at 8 kV (He); NRMS recorded on Zab 2F at 8 kV (Xe/O).

the structure of the starting material (**1**), this clear differentiation demonstrates that the *m/z* 59 ions formed by fragmentation of **1** have the structure $H{-}C{\equiv}N{\rightarrow}S^{+\cdot}$.

Proof of the existence of the neutral molecule, $H{-}C{\equiv}N{\rightarrow}S$, was obtained by NRMS.

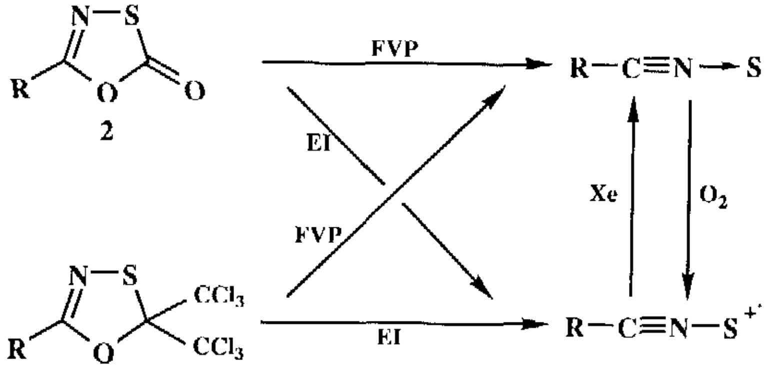
As expected, the NRMS of the $H{-}N{=}C{=}S^{+\cdot}$ ions from isothiocyanic acid regenerates the original mass spectrum, featuring signals at *m/z* 27, 32, and 44 (Figure 1c). The NRMS of the ions $H{-}C{\equiv}N{-}S^{+\cdot}$ produced from **1** likewise regenerates a strong survivor signal at *m/z* 59, closely resembling the CA spectrum and in particular still featuring the characteristic peak at *m/z* 46 (NS) (Figure 1d). These observations clearly demonstrate that neutral $H{-}C{\equiv}N{\rightarrow}S$ retains its structural identity and does not isomerize to $H{-}N{=}C{=}S$ on the microsecond time scale of the NRMS experiment.

Several other CHNS precursors were examined. The molecular ions of 3–amino– and 3–methyl–1,2,4–triazole–5–thiol, trithiocyanuric acid, ethyl thiocyanate and ethyl isothiocyanate all gave $H{-}N{=}C{=}S^{+\cdot}$ ions exclusively, as identified by their CAMS which were identical with that shown in Figure 1a. Thus, compound **1** is unique in generating thiofulminic acid, $H{-}C{\equiv}N{\rightarrow}S$.

We have demonstrated elsewhere the formation of the molecular ions of benzonitrile sulfide from five different precursors, as well as the NRMS to the neutral, $Ph{-}C{\equiv}N{\rightarrow}S$.[9] Moreover, $Ph{-}C{\equiv}N{\rightarrow}S$ is formed as a discrete gas phase molecule on flash vacuum pyrolysis (FVP) of the oxathiazole derivatives **2a** and **3a** at 550°C and is now identified not only by its NRMS but also by Ar matrix isolation at 12 K, where the $-C{\equiv}N{-}S$ stretch is observed at 2185 cm^{-1}. Although partial decomposition to benzonitrile and sulfur takes place under these conditions, and this process is completed by bleaching of the matrix with 335 nm light, the experiment demonstrates the existence of $Ph{-}C{\equiv}N{\rightarrow}S$ with lifetimes of the order of milliseconds in the gas phase.[10]

The electron ionization (EI) mass spectra of the methyl oxathiazoles **2b** and **3b** feature strong signals at *m/z* 73, corresponding to $CH_3{-}C{\equiv}N{-}S^{+\cdot}$. These ions were differentiated from those of $CH_3{-}N{=}C{=}S$ and $CH_3{-}S{-}C{\equiv}N$ by kinetic energy release, metastable ion, and collision activation mass spectrometry. While all three ions show a loss of a methyl group (giving *m/z* 58) in the CAMS, $CH_3{-}N{=}C{=}S$ alone features strong signals at *m/z* 44 and 45, $CH_3{-}S{-}C{\equiv}N$ at *m/z* 45 and 46, and the *m/z* 73 ions produced from **2b** and **3b** give strong signals at *m/z* 46 and 47, 32 (S), and 38–41 (CH_3CN). The differences are preserved in the NR mass spectra, whereby the *m/z* 73 signal surviving the NRMS experiment is significantly weaker for the ion originating from **2b** than for the stable molecules CH_3NCS and CH_3SCN.

Mass spectrometric monitoring of the flash vacuum pyrolyses of **2b** and **3b** demonstrated the formation of CH_3CN as the starting materials decomposed at 300–500°C. In addition, CO_2 was formed from **2b**, and hexachloroacetone (identified by the CCl_3 signal) from **3b**. The *m/z* 73 signals decreased at the same rates as the molecular ions of the starting materials, indicating that $CH_3{-}C{\equiv}N{\rightarrow}S$ is thermally less stable than $Ph{-}C{\equiv}N{\rightarrow}S$. Interestingly, the *m/z* 64 (S_2) signals showed a stronger increase with temperature than did *m/z* 32 (S), in analogy with our previous observation that N_2S decomposes



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3 a : R = C_6H_5
b : R = CH_3

to N_2 and S_2.[3a,b] The matrix isolation of $CH_3–C≡N→S$ from a thermal system may therefore be expected to be difficult. Preliminary experiments on the FVP of **3b** at 300–500°C gave rise to a new peak at 2230 cm^{-1} in the IR spectrum (Ar, 12 K), which is bleached by UV light. Further work aimed at a full characterization of $CH_3–C≡N→S$ will be reported.

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