Kurzmitteilung / Short Communication

Characterization of Neutral and Ionic Sulfur–Nitrogen Cluster Molecules NS_2 and NS_3 in the Gas Phase

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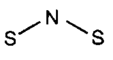
Collision experiments on NS_x^- (x = 2, 3) clusters are reported. Evidence is presented for the gas-phase existence of the corresponding NS_x and NS_x^+ species. For x = 3, the mass spectra are very much in keeping with a connectivity SS–NS (**5**) for all three charge states. For x = 2, the experimental data favor the presence of NSS (**2**); however, the cyclic C_{2v}-symmetric form **3** cannot be ruled out.

The continuing interest in the theoretical and experimental characterization of trioxides (XO_3) and trisulfides (XS_3) of the main-group elements is due to the particular electronic and structural properties assigned to these species. While there exist several reports on the trioxides of carbon (CO_3)[1], silicon (SiO_3)[2], nitrogen (NO_3)[3], phosphorus (PO_3)[4], and since recently on the generation and identification of the trisulfides of carbon (CS_3)[5] and phosphorus (PS_3)[6], much less, however, is known about the nitrogen–sulfur species N_xS_y. For example, data on the successful gas-phase characterization of the analogous nitrogen trisulfide NS_3 are to our knowledge not available in the literature.

$(SN)_x$ oligomers with $x = 2-4$ are known to be formed by evaporation of polymeric polythiazyl (SN) and have been examined by matrix infrared spectroscopy[7]. Other nitrogen sulfides such as NS and N_2S were characterized by spectroscopic and mass-spectrometric techniques[8a]. Ab initio calculations[9a] and correlations with measured matrix infrared absorptions, photoelectron spectra and high-resolution IR[8a] have now firmly established that N_2S possesses a linear structure with a rather weak nitrogen–sulfur bond.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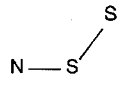
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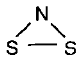
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N—S — S—S

4

S—S — N—S

5

In microwave discharge experiments of a mixture of CS_2 and N_2 an NS_2 species was thought to be produced by analyzing the isotopic substitution pattern of the measured microwave spectra[8b]. In a very recent study, Hassanzadeh and Andrews[8a] examined several nitrogen sulfides formed in a microwave discharge of a mixture of nitrogen and sulfur vapor. The authors trapped the different species formed in this process in solid argon and recorded the infrared spectra for SNS (**1**), NS_2 (**2**) and higher sulfides. In line with ab initio calculations on the $[N,S_2]$ surface carried out by Schaefer et al.[9b] the symmetrical C_{2v} isomer **1** was found to be formed in the matrix study. Interestingly, however, the asymmetric NSS isomer **2**, which lies 19 kcal/mol higher in energy than **1** and which upon UV radiation rearranges to the more stable SNS isomer **1**, was also observed in the matrix. The authors[8a] explained the relatively high initial abundance of this species **2** by two possible reaction pathways (I and II) that lead to the energetically less stable isomer under matrix-isolation conditions.

$$N + S_2 \rightarrow N{-}S{-}S \qquad (I)$$

$$NS + S \rightarrow N{-}S{-}S \qquad (II)$$

In a further theoretical study Sannigrahi and Peyerimhoff[9c,d] calculated the ionization energy and electron affinity of the C_{2v}-symmetric SNS radical (full CI calculations). The authors reported the SNS^- ion to possess a structure **1** with an SNS bond angle of 123.2°. Upon electron detachment this species was calculated to form an SNS molecule with a bond angle of 151.5° and further electron removal was found to lead to the linear SNS^+ ion with $D_{\infty h}$ symmetry. The low-lying linear and bent quadruplet states and thus the electronic spectrum of the SNS molecule have been calculated by Schaefer et al.[9e]. The NS_2^- ion is also believed to be an intermediate in the formation of NS_4^- from $N_3S_3^-$[10a]. In the matrix study by Hassanzadeh and Andrews[8a] the authors also reported the NS_3 species **4** to be formed in the matrix. This molecule was detected by increasing the amount of sulfur in the discharge experiments. The NS_3 species was identified as **4** on the basis of an analysis of the isotopic pattern of the sulfur–sulfur vibrations. Upon UV irradiation the molecule was found to decompose into NS and S_2, and no possible rearrangement products (as for example **4** → **5**) were observed. Thus, the authors assigned a structure possessing an NS and an SS subunit with a rather weak sulfur–sulfur interaction between the two parts of the molecule. The NS_3^- anion was observed in a ^{14}N-NMR study of a mixture of HNS_7 and KNH_2 in liquid ammonia[10b]. However, no structural information was re-

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ported. Experimental evidence for the formation of an SN−S$_2$ molecule with a structure **5** does not seem to exist.

In this paper we report on the results of gas-phase experiments with nitrogen disulfide, NS$_2$, and nitrogen trisulfide, NS$_3$, cluster molecules. We have applied the techniques of neutralization-reionization (NR)[11] and charge-reversal (CR)[12] mass spectrometry to study the fragmentation behavior of the cluster molecules in high-energy collisions. As has been demonstrated in a number of cases[13], the NRMS technique can provide valuable information on the existence and unimolecular fragmentation processes of such small cluster molecules.

The collision experiments were carried out on a modified four-sector tandem mass spectrometer with *BEBE* modification (*B* stands for magnetic and *E* for electrostatic analyzer). A detailed descriptrion of the experimental setup has been given in previous publications[14]. In brief, the *anionic* cluster molecules can be readily obtained from a mixture of N$_2$ or N$_2$O and COS in a CI ion source. The gas mixture was bombarded with electrons possessing 70 eV energy (repeller voltage ca. 0 V; ion-source temperature 200°C, acceleration voltage 8 kV). The ions were accelerated to 8-keV kinetic energy and mass-selected by means of *B*1/*E*1 (mass resolution $m/\Delta m$ = 3000. In the case of the CR experiments they were then collided with oxygen in the second part of a differentially pumped tandem-collision cell and the so-obtained charge-reversed ions were recorded by scanning *B*2. For the $^-$NR$^+$ experiments also the first part of the collision cell was flooded with oxygen, and a deflector electrode situated between the two collision cells was charged to 1000 V. (Experiments in which the *anionic* precursor is neutralized and in a subsequent collision oxidized to the corresponding *cationic* species are abbreviated as $^-$NR$^+$ experiments[11].) Thus, only neutralized molecules are enabled to pass into the second cell. For a particle of *m/z* 110, having been accelerated to 8-keV energy, it takes approximately 10 microseconds to travel from the first to the second collision cell, thus providing a lower limit for the *minimal* lifetime of the neutral molecule. The ionic dissociation products were recorded by scanning the second magnetic analyzer (*B*2). To improve the signal-to-noise ratio of the spectra the data of 10−30 accumulated scans were processed on-line with an AMD Intectra data system.

The $^-$NR$^+$ spectra of the anionic cluster molecules NS$_2^-$ and NS$_3^-$ are given in Figures 1 and 2. The presence of intense recovery signals for both species reflects both the stability of the neutral molecules and favorable Franck-Condon factors for the vertical[15] electron-transfer reactions: NS$_x^-$ → NS$_x$ → NS$_x^+$ (x = 2, 3).

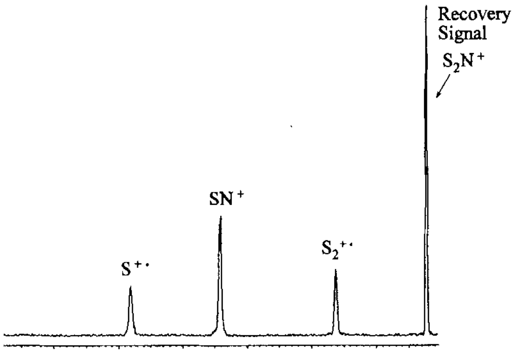

Figure 1. Neutralization-reionization ($^-$NR$^+$) mass spectrum of NS$_2^-$ (oxygen, 80% transmission *T* // oxygen 80% *T*)

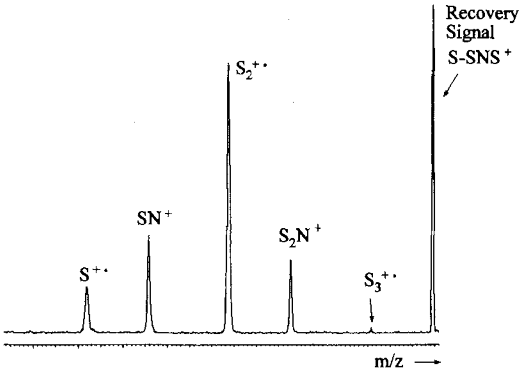

Figure 2. $^-$NR$^+$ mass spectrum of NS$_3^-$ (oxygen 80% *T* // oxygen 80% *T*)

The fragmentation pattern of the reionized NS$_2$ can be rationalized by a structure possessing an NSS connectivity **2**. This view is evidenced by the strong signal for the S$_2^{+\bullet}$ ion. On thermodynamical grounds both the production of NS$^+$ and the S$_2^{+\bullet}$ formation are practically equally favored[16]. While a cyclic NS$_2$ structure **3** cannot be totally ruled out on the basis of the collision experiment, a bent species possessing C_{2v} symmetry as depicted in structure **1** is probably not formed in our experiment. This view is further supported by a CA experiment (not shown) of the ion NS$_2^-$ where the S$_2^-$ signal corresponds to the strongest fragment. Unfortunately, thermochemical data regarding the heat of formation of the relevant fragment species are not available in the literature.

The $^-$NR$^+$ spectrum for the NS$_3$ species can be explained by an SN−SS connectivity (structure **5**). Practically, no S$_3^+$ signal is observed, thus indicating the molecule to consist of an NS and an SS subunit with no S$_3$ building block. This view is further supported by an additional CA experiment of the *anionic* precursor. The SNSS anion does practically not give rise to any S$_3^-$ fragments; rather, strong S$_2^-$ and NS$^-$ signals are recorded. As the electron affinity of S$_3$ is with a value of 2.09 eV[16] approximately 0.43 eV higher than that of S$_2$, the ion possessing an N−S−S−S connectivity **4** should give rise to S$_3^-$ as an observable product in the CA process. The heat of formation for the two possible product pairs in this fragmentation processes (NS$_3^-$ → S$_3^-$/N; $\Sigma\Delta H_f^0$ = 53 ± 11 kcal/mol and NS$_3^-$ → S$_2^-$/NS; $\Sigma\Delta H_f^0$ = 31 ± 30 kcal/mol)[16] is of the same order of magnitude, considering the large error limits given with both experimental values. Thus, both fragmentation processes should be of rather similar intensity if the examined anion had possessed an N−S−S−S connectivity **4**. The charge reversal spectra corresponding to a one-collision double-electron transfer process are depicted in Figures 3 and 4. They further support the proposed structural assignments made after analyzing the NRMS data. The only major difference is observed in the stronger NS$_2^+$

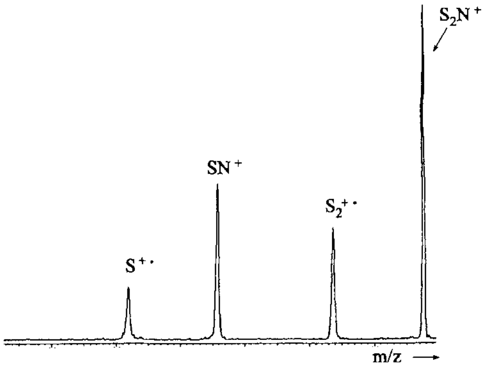

Figure 3. Charge reversal (CR) mass spectrum of NS$_2^-$ (oxygen 80% *T*)

fragment in the case of the SNSS spectrum (Figure 4). The weaker formation of NS_2^+ over S_2^+ in the case of the $^-NR^+$ experiment can be the result of a relatively weak bonding between the NS and SS subunits in the neutral molecule.

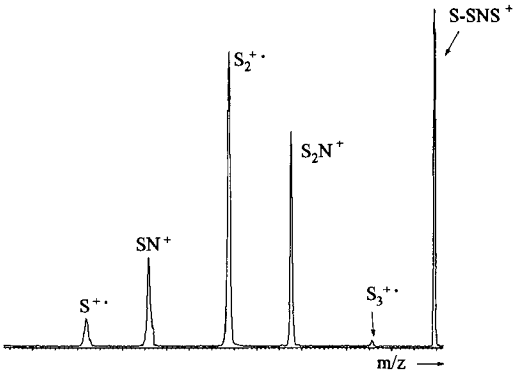

Figure 4. CR mass spectrum of NS_3^- (oxygen 80% *T*)

While in the case of the neutral NS_2 an unambiguous structural distinction between the bent asymmetric species **2** and the cyclic isomer **3** based on the collision spectra cannot be made, experimental evidence was found for the nitrogen trisulfide, NS_3, cluster molecule to possess an SN–SS connectivity as depicted in structure **5**[17].

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[17] The possibility that NS_3 may possess a C_{3v}-symmetric trithionitrate-like connectivity is discarded on the ground that such a structure would not account for the increased formation of S_2^+ in the $^-NR^+$ experiment of NS_3^-; rather, a stronger NS_2^+ signal would be expected.

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